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ANALYSIS OF  
PAINT VEHICLES, JAPANS  
AND VARNISHES



# ANALYSIS OF PAINT VEHICLES, JAPANS AND VARNISHES

BY

CLIFFORD DYER HOLLEY, M.S., PH.D.

PROFESSOR CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN  
AND CHIEF CHEMIST ACME WHITE LEAD & COLOR WORKS

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## PREFACE

THE great progress in the development of the Paint, Enamel and Varnish Industries which has marked the past decade has brought with it an urgent necessity for systematic methods of analysis, particularly with reference to the vehicles used. Due to the increased number of technical men working in these industries, great advances have been made in the discovery, processing and utilization of a number of oils, and other vehicles which have not heretofore found extended use in the paint and varnish trade.

The methods of analysis here presented are essentially those used by the author in his laboratory work. Many of them are the results of extended investigation conducted by him and his associates, others represent the best thought of representative technologists, and have been adopted as standard methods by the American Society For Testing Materials.

In the arrangement and presentation of the subject matter, the needs of the analyst have been kept constantly in view, and it is the hope of the author that this book will prove of material value to all those engaged in the manufacture and examination of paint, enamel and varnish products.

CLIFFORD D. HOLLEY

DETROIT, MICHIGAN

*October 10, 1919*





# CONTENTS

CHAPTER	PAGE
I. EXAMINATION OF PETROLEUM THINNERS . . . . .	1
II. EXAMINATION OF PETROLEUM THINNERS ( <i>continued</i> ) . . . . .	14
III. EXAMINATION OF TURPENTINE . . . . .	28
IV. ALCOHOLS AND ACETONES . . . . .	35
V. BENZOL AND SOLVENT NAPHTHAS . . . . .	49
VI. LINSEED OIL . . . . .	52
VII. LINSEED OIL ( <i>continued</i> ) . . . . .	65
VIII. TUNG OIL (CHINESE WOOD OIL) . . . . .	79
IX. MISCELLANEOUS PAINT AND VARNISH OILS . . . . .	91
X. SEPARATION OF VEHICLE FROM PIGMENT . . . . .	96
XI. ESTIMATION OF WATER IN PAINTS . . . . .	105
XII. WATER EMULSIONS AND EMULSIFIERS . . . . .	109
XIII. DETERMINATION OF VOLATILE THINNER . . . . .	115
XIV. EXAMINATION OF THE EXTRACTED OIL . . . . .	122
XV. EFFECT OF STORAGE ON THE COMPOSITION OF PAINTS . . . . .	131
XVI. ANALYSIS OF SOLID AND LIQUID DRIERS . . . . .	138
XVII. COMPARATIVE ANALYSIS OF BLACK BAKING JAPANS . . . . .	154
XVIII. ANALYSIS OF SHELLAC AND LACQUERS . . . . .	167
XIX. ANALYSIS OF VARNISH AND ENAMEL LIQUIDS . . . . .	180
XX. ANALYSIS OF VARNISH AND ENAMEL LIQUIDS ( <i>continued</i> ) . . . . .	189
ADDENDA . . . . .	196
INDEX . . . . .	197



# ANALYSIS OF PAINT VEHICLES JAPANS AND VARNISHES

## CHAPTER I

### EXAMINATION OF PETROLEUM THINNERS

1. The enormous increase, during the past ten years, in the use of petroleum thinners in the manufacture of paints and varnishes, both for general and special uses, and the successful results obtained with them necessitate on the part of the chemist a thorough and consistent procedure of examination of this class of products. The methods adopted should be rapid and at the same time yield results that can be closely duplicated, not only by the same operator, but by others.

2. **Odor.** All petroleum naphthas or turpentine substitutes should have a pleasant and agreeable odor. A penetrating disagreeable odor, suggestive of sulphur compounds, or a strong gaseous odor becomes highly intensified when such products are used as components of paints or enamels and allowed to remain in sealed packages for some time. A sample or shipment having a questionable odor should be placed in a closed can or flask, allowing considerable air space, and kept for at least three days in a warm place. If the odor has become materially stronger

(1) Odor  
T-3

and more disagreeable in character, the sample or shipment should be regarded unfavorably.

7-2  
(2) Color

3. Color. The color should be water white, have no yellow cast or evidence of a bloom. This is best observed by placing side by side in 500-c.c. beakers, on a white surface, samples of the material to be tested and the standard.

7-31  
(3) Solvent Strength

4. Solvent strength. It is well known that petroleum thinners having substantially the same distillation figures may vary greatly in their ability to hold in solution the varnish gums. In the manufacture and use of varnishes made without turpentine it is necessary to select petroleum thinners of the greatest solvent strength consistent with the working, drying and other necessary features.

Kauri Varnish  
1 lb. Kauri  
8 7/16 ozs linseed oil  
1/4 gal turp Subst.

A definite and practical test for the solvent strength of any petroleum thinner may be made by selecting a short oil kauri varnish containing no turpentine; for example, one made from 100 lbs. kauri, 7 gals. of linseed oil and 25-30 gals. of an accepted turpentine substitute. The method of procedure used by the author is as follows: Pour into a 6-oz. graduate 2 oz. of the varnish. Add carefully, by allowing to flow down the side of the graduate so as not to mix with the varnish, 2 oz. of the thinner to be tested. The two layers are now mixed by vigorous stirring; a slight break may be noticed, but the thinner should dissolve the broken-out portion without difficulty. If the thinner stands this test, further additions of the thinner in  $\frac{1}{2}$ -oz. portions should be made in the same manner till a permanent break is obtained. If properly conducted the above test will give very accurate information as to the solvent strength of any thinner. It is, however, necessary to take a few

simple precautions, such as keeping the temperature constant, and adopting a strictly uniform procedure for the addition of the thinner to be tested.

In conducting the above test a freshly drawn sample of varnish should be used, or else the varnish should be kept in a completely filled can, as continued exposure to the air, such as occurs in a partially filled package, materially affects the solubility of the gum.

Many of the complaints received from the users of varnish and enamel products are caused by the gradual breaking out of the gums from solution. Often two to six months will elapse before the deterioration is observable; primarily it is due to the use of thinners of low solvent strength and, therefore, in the testing a generous margin of safety should be observed.

**5. Specific gravity.** The manufacturers of petroleum products use the Beaumé scale exclusively. The chemist, therefore, should be provided with an accurate set of Tagliabue hydrometers, including the following:

19° to 31° Bé.	equivalent to	0.9402 to 0.8708 Sp. Gr.
29° " 41° "	" "	0.8816 " 0.8203 " "
39° " 51° "	" "	0.8299 " 0.7753 " "
49° " 61° "	" "	0.7839 " 0.7351 " "

The gravity is determined without cooling and the temperature correction made according to the following tables. At 60° F. the indications of the hydrometer require no correction; below that temperature the indications are too low, above it, too high. Suppose the hydrometer reads 54° Bé. and thermometer 40° F., the corrected reading of 56.1° Bé. for 60° F. is found in the temperature column under 40° and opposite the indication 54. If the reading is desired in terms of specific gravity, Table II may be used.

(4) Specific Gravity.  
T-6

This table is the one according to which the Tagliabue hydrometers are made, being based on the formula

$$\text{S.G.} = \frac{141.5}{131.5 + B},$$

and is the one universally used by the petroleum manufacturers and refiners. Lately the modulus 140, as expressed by the formula

$$\text{S.G.} = \frac{140}{130 + B},$$

has been urged. The oil trade, however, has shown little, if any, disposition to adopt it.



TABLE I  
6. Temperature Corrections

*Ent. Book*

Indication	TEMPERATURES									
	40°	41°	42°	43°	44°	45°	46°	47°	48°	49°
15	16.0	16.0	15.9	15.9	15.8	15.8	15.7	15.7	15.6	15.6
16	17.1	17.1	17.0	16.9	16.9	16.8	16.8	16.7	16.6	16.6
17	18.1	18.1	18.0	17.9	17.9	17.8	17.8	17.7	17.6	17.6
18	19.1	19.1	19.0	18.9	18.9	18.8	18.8	18.7	18.6	18.6
19	20.1	20.1	20.0	19.9	19.9	19.8	19.8	19.7	19.6	19.6
20	21.1	21.0	21.0	20.9	20.9	20.8	20.7	20.7	20.6	20.6
21	22.1	22.1	22.0	21.9	21.9	21.8	21.8	21.7	21.6	21.6
22	23.2	23.1	23.0	23.0	22.9	22.8	22.8	22.7	22.7	22.6
23	24.2	24.1	24.1	24.0	23.9	23.9	23.8	23.7	23.7	23.6
24	25.2	25.2	25.1	25.0	25.0	24.9	24.8	24.8	24.7	24.6
25	26.3	26.2	26.1	26.1	26.0	25.9	25.8	25.8	25.7	25.6
26	27.3	27.2	27.2	27.1	27.0	26.9	26.9	26.8	26.7	26.7
27	28.3	28.2	28.2	28.1	28.0	28.0	27.9	27.8	27.8	27.7
28	29.3	29.3	29.2	29.1	29.1	29.0	28.9	28.8	28.8	28.7
29	30.4	30.3	30.2	30.1	30.1	30.0	29.9	29.9	29.8	29.7
30	31.4	31.3	31.2	31.2	31.1	31.0	31.0	30.9	30.8	30.7
31	32.4	32.4	32.3	32.2	32.1	32.1	32.0	31.9	31.8	31.8
32	33.5	33.4	33.3	33.2	33.1	33.1	33.0	32.9	32.9	32.8
33	34.5	34.4	34.3	34.2	34.2	34.1	34.0	34.0	33.9	33.8
34	35.5	35.4	35.4	35.3	35.2	35.1	35.1	35.0	34.9	34.8
35	36.5	36.5	36.4	36.3	36.2	36.2	36.1	36.0	35.9	35.8
36	37.6	37.5	37.4	37.3	37.2	37.2	37.1	37.0	36.9	36.8
37	38.6	38.5	38.4	38.3	38.3	38.2	38.1	38.0	37.9	37.9
38	39.6	39.5	39.4	39.4	39.3	39.2	39.1	39.0	39.0	38.9
39	40.6	40.5	40.5	40.4	40.3	40.2	40.1	40.1	40.0	39.9
40	41.6	41.6	41.5	41.4	41.3	41.2	41.2	41.1	41.0	40.9
41	42.7	42.6	42.5	42.4	42.3	42.3	42.2	42.1	42.0	41.9
42	43.7	43.6	43.5	43.4	43.4	43.3	43.2	43.1	43.0	42.9
43	44.7	44.6	44.5	44.5	44.4	44.3	44.2	44.1	44.0	44.0
44	45.7	45.7	45.6	45.5	45.4	45.3	45.2	45.2	45.1	45.0
45	46.8	46.7	46.6	46.5	46.4	46.3	46.3	46.2	46.1	46.0
46	47.8	47.7	47.6	47.5	47.4	47.3	47.3	47.2	47.1	47.0
47	48.8	48.7	48.6	48.6	48.5	48.4	48.3	48.2	48.1	48.0
48	49.9	49.8	49.7	49.6	49.5	49.4	49.3	49.2	49.1	49.0
49	50.9	50.8	50.7	50.6	50.5	50.4	50.3	50.2	50.1	50.0
50	52.0	51.9	51.8	51.7	51.6	51.5	51.4	51.3	51.2	51.1
51	53.0	52.9	52.8	52.7	52.6	52.5	52.4	52.3	52.2	52.1
52	54.0	53.9	53.8	53.7	53.6	53.5	53.4	53.3	53.2	53.1
53	55.1	55.0	54.9	54.8	54.6	54.5	54.4	54.3	54.2	54.1
54	56.1	56.0	55.9	55.8	55.7	55.6	55.5	55.4	55.2	55.1
55	57.1	57.0	56.9	56.8	56.7	56.6	56.5	56.4	56.3	56.2
56	58.2	58.1	58.0	57.9	57.8	57.7	57.5	57.4	57.3	57.2
57	59.2	59.1	59.0	58.9	58.8	58.7	58.5	58.4	58.3	58.2
58	60.3	60.1	60.0	59.9	59.8	59.7	59.6	59.4	59.3	59.2
59	61.3	61.2	61.1	61.0	60.8	60.7	60.6	60.5	60.4	60.2
60	62.3	62.2	62.1	62.0	61.9	61.7	61.6	61.5	61.4	61.3

Indication	TEMPERATURES									
	50°	51°	52°	53°	54°	55°	56°	57°	58°	59°
15	15.5	15.5	15.4	15.4	15.3	15.3	15.2	15.2	15.1	15.1
16	16.5	16.5	16.4	16.4	16.3	16.3	16.2	16.2	16.1	16.1
17	17.5	17.5	17.4	17.4	17.3	17.3	17.2	17.2	17.1	17.1
18	18.5	18.5	18.4	18.4	18.3	18.3	18.2	18.2	18.1	18.1
19	19.5	19.5	19.4	19.4	19.3	19.3	19.2	19.2	19.1	19.1
20	20.5	20.5	20.4	20.4	20.3	20.3	20.2	20.2	20.1	20.1
21	21.5	21.5	21.4	21.4	21.3	21.3	21.2	21.2	21.1	21.1
22	22.5	22.5	22.4	22.4	22.3	22.3	22.2	22.2	22.1	22.1
23	23.6	23.5	23.5	23.4	23.4	23.3	23.2	23.2	23.1	23.1
24	24.6	24.5	24.5	24.4	24.4	24.3	24.3	24.2	24.1	24.1
25	25.6	25.5	25.5	25.4	25.4	25.3	25.3	25.2	25.1	25.1
26	26.6	26.5	26.5	26.4	26.4	26.3	26.3	26.2	26.1	26.1
27	27.6	27.6	27.5	27.4	27.4	27.3	27.3	27.2	27.1	27.1
28	28.6	28.6	28.5	28.4	28.4	28.3	28.3	28.2	28.1	28.1
29	29.7	29.6	29.5	29.5	29.4	29.3	29.3	29.2	29.1	29.1
30	30.7	30.6	30.5	30.5	30.4	30.3	30.3	30.2	30.1	30.1
31	31.7	31.6	31.6	31.5	31.4	31.3	31.3	31.2	31.1	31.1
32	32.7	32.6	32.6	32.5	32.4	32.4	32.3	32.2	32.1	32.1
33	33.7	33.7	33.6	33.5	33.4	33.4	33.3	33.2	33.2	33.1
34	34.8	34.7	34.6	34.5	34.5	34.4	34.3	34.2	34.2	34.1
35	35.8	35.7	35.6	35.5	35.5	35.4	35.3	35.2	35.2	35.1
36	36.8	36.7	36.6	36.5	36.5	36.4	36.3	36.2	36.2	36.1
37	37.8	37.7	37.6	37.5	37.5	37.4	37.3	37.2	37.2	37.1
38	38.8	38.7	38.6	38.6	38.5	38.4	38.3	38.2	38.2	38.1
39	39.8	39.7	39.7	39.6	39.5	39.4	39.3	39.2	39.2	39.1
40	40.8	40.7	40.7	40.6	40.5	40.4	40.3	40.2	40.2	40.1
41	41.8	41.8	41.7	41.6	41.5	41.4	41.3	41.2	41.2	41.1
42	42.9	42.8	42.7	42.6	42.5	42.4	42.3	42.3	42.2	42.1
43	43.9	43.8	43.7	43.6	43.5	43.4	43.3	43.3	43.2	43.1
44	44.9	44.8	44.7	44.6	44.5	44.4	44.4	44.3	44.2	44.1
45	45.9	45.8	45.7	45.6	45.5	45.5	45.4	45.3	45.2	45.1
46	46.9	46.8	46.7	46.6	46.6	46.5	46.4	46.3	46.2	46.1
47	47.9	47.8	47.7	47.7	47.6	47.5	47.4	47.3	47.2	47.1
48	48.9	48.9	48.8	48.7	48.6	48.5	48.4	48.3	48.2	48.1
49	50.0	49.9	49.8	49.7	49.6	49.5	49.4	49.3	49.2	49.1
50	51.0	50.9	50.8	50.7	50.6	50.5	50.4	50.3	50.2	50.1
51	52.0	51.9	51.8	51.7	51.6	51.5	51.4	51.3	51.2	51.1
52	53.0	52.9	52.8	52.7	52.6	52.5	52.4	52.3	52.2	52.1
53	54.0	53.9	53.8	53.7	53.6	53.5	53.4	53.3	53.2	53.1
54	55.0	54.9	54.8	54.7	54.6	54.5	54.4	54.3	54.2	54.1
55	56.1	56.0	55.9	55.8	55.7	55.5	55.4	55.3	55.2	55.1
56	57.1	57.0	56.9	56.8	56.7	56.5	56.4	56.3	56.2	56.1
57	58.1	58.0	57.9	57.8	57.7	57.5	57.4	57.3	57.2	57.1
58	59.1	59.0	58.9	58.8	58.7	58.5	58.4	58.3	58.2	58.1
59	60.1	60.0	59.9	59.8	59.7	59.6	59.5	59.3	59.2	59.1
60	61.1	61.0	60.9	60.8	60.7	60.6	60.5	60.3	60.2	60.1

Indication	TEMPERATURES									
	60°	61°	62°	63°	64°	65°	66°	67°	68°	69°
15	15.0	15.0	14.9	14.8	14.8	14.7	14.7	14.6	14.5	14.5
16	16.0	16.0	15.9	15.8	15.8	15.7	15.7	15.6	15.5	15.5
17	17.0	17.0	16.9	16.8	16.8	16.7	16.7	16.6	16.5	16.5
18	18.0	18.0	17.9	17.8	17.8	17.7	17.7	17.6	17.5	17.5
19	19.0	19.0	18.9	18.8	18.8	18.7	18.7	18.6	18.5	18.5
20	20.0	19.9	19.9	19.8	19.8	19.7	19.6	19.6	19.5	19.5
21	21.0	20.9	20.9	20.8	20.7	20.7	20.6	20.6	20.5	20.4
22	22.0	21.9	21.9	21.8	21.7	21.7	21.6	21.5	21.5	21.4
23	23.0	22.9	22.9	22.8	22.7	22.7	22.6	22.5	22.5	22.4
24	24.0	23.9	23.9	23.8	23.7	23.7	23.6	23.5	23.5	23.4
25	25.0	24.9	24.9	24.8	24.7	24.7	24.6	24.5	24.5	24.4
26	26.0	25.9	25.9	25.8	25.7	25.7	25.6	25.5	25.5	25.4
27	27.0	26.9	26.9	26.8	26.7	26.7	26.6	26.5	26.5	26.4
28	28.0	25.9	27.9	27.8	27.7	27.7	27.6	27.5	27.5	27.4
29	29.0	28.9	28.9	28.8	28.7	28.7	28.6	28.5	28.5	28.4
30	30.0	29.9	29.9	29.8	29.7	29.7	29.6	29.5	29.5	29.4
31	31.0	30.9	30.9	30.8	30.7	30.6	30.6	30.5	30.4	30.4
32	32.0	31.9	31.9	31.8	31.7	31.6	31.6	31.5	31.4	31.4
33	33.0	32.9	32.8	32.8	32.7	32.6	32.6	32.5	32.4	32.4
34	34.0	33.9	33.8	33.8	33.7	33.6	33.5	33.5	34.4	33.3
35	35.0	34.9	34.8	34.8	34.7	34.6	34.5	34.5	34.4	34.3
36	36.0	35.9	35.8	35.8	35.7	35.6	35.5	35.5	35.4	35.3
37	37.0	36.9	36.8	36.8	36.7	36.6	36.5	36.5	36.4	36.3
38	38.0	37.9	37.8	37.8	37.7	37.6	37.5	37.5	37.4	37.3
39	39.0	38.9	38.8	38.8	38.7	38.6	38.5	38.4	38.4	38.3
40	40.0	39.9	39.8	39.8	39.7	39.6	39.5	39.4	39.4	39.3
41	41.0	40.9	40.8	40.8	40.7	40.6	40.5	40.4	40.3	40.3
42	42.0	41.9	41.8	41.7	41.7	41.6	41.5	41.4	41.3	41.3
43	43.0	42.9	42.8	42.7	42.7	42.6	42.5	42.4	42.3	42.2
44	44.0	43.9	43.8	43.7	43.6	43.6	43.5	43.4	43.3	43.2
45	45.0	44.9	44.8	44.7	44.6	44.6	44.5	44.4	44.3	44.2
46	46.0	45.9	45.8	45.7	45.6	45.5	45.5	45.4	45.3	45.2
47	47.0	46.9	46.8	46.7	46.6	46.5	46.5	46.4	46.3	46.2
48	48.0	47.9	47.8	47.7	47.6	47.5	47.4	47.4	47.3	47.2
49	49.0	48.9	48.8	48.7	48.6	48.5	48.4	48.3	48.3	48.2
50	50.0	49.9	49.8	49.7	49.6	49.5	49.4	49.3	49.2	49.1
51	51.0	50.9	50.8	50.7	50.6	50.5	50.4	50.3	50.2	50.1
52	52.0	51.9	51.8	51.7	51.6	51.5	51.4	51.3	51.2	51.1
53	53.0	52.9	52.8	52.7	52.6	52.5	52.4	52.3	52.2	52.1
54	54.0	53.9	53.8	53.7	53.6	53.5	53.4	53.3	53.2	53.1
55	55.0	54.9	54.8	54.7	54.6	54.5	54.4	54.3	54.2	54.1
56	56.0	55.9	55.8	55.7	55.6	55.5	55.4	55.3	55.2	55.1
57	57.0	56.9	56.8	56.7	56.6	56.5	56.4	56.2	56.1	56.0
58	58.0	57.9	57.8	57.7	57.6	57.5	57.3	57.2	57.1	57.0
59	59.0	58.9	58.8	58.7	58.6	58.5	58.3	58.2	58.1	58.0
60	60.0	59.9	59.8	59.7	59.6	59.4	59.3	59.2	59.1	59.0



Indication	TEMPERATURES									
	70°	71°	72°	73°	74°	75°	76°	77°	78°	79°
15	14.4	14.4	14.3	14.3	14.2	14.2	14.2	14.1	14.1	14.0
16	15.4	15.4	15.3	15.3	15.2	15.2	15.2	15.1	15.1	15.0
17	16.4	16.4	16.3	16.3	16.2	16.2	16.1	16.1	16.0	16.0
18	17.4	17.4	17.3	17.3	17.2	17.2	17.1	17.1	17.0	17.0
19	18.4	18.4	18.3	18.3	18.2	18.2	18.1	18.1	18.0	18.0
20	19.4	19.3	19.3	19.2	29.2	19.1	19.1	19.0	19.0	18.9
21	20.4	20.3	20.3	20.2	20.2	20.1	20.0	20.0	19.9	19.9
22	21.4	21.3	21.3	21.2	21.1	21.1	21.0	21.0	20.9	20.9
23	22.4	22.3	22.3	22.2	22.1	22.1	22.0	22.0	21.9	21.8
24	23.4	23.3	23.2	23.2	23.1	23.1	23.0	22.9	22.9	22.8
25	24.3	24.3	24.2	24.2	24.1	24.0	24.0	23.9	23.9	23.8
26	25.3	25.3	25.2	25.1	25.1	25.0	25.0	24.9	24.8	24.8
27	26.3	26.3	26.2	26.1	26.1	26.0	25.9	25.9	25.8	25.7
28	27.3	27.3	27.2	27.1	27.1	27.0	26.9	26.9	26.8	26.7
29	28.3	28.3	28.2	28.1	28.1	28.0	27.9	27.8	27.8	27.7
30	29.3	29.2	29.2	29.1	29.0	29.0	28.9	28.8	28.8	28.7
31	30.3	30.2	30.2	30.1	30.0	29.9	29.9	29.8	29.7	29.7
32	31.3	31.2	31.2	31.1	31.0	30.9	30.9	30.8	30.7	30.6
33	32.3	32.2	32.1	32.1	32.0	31.9	31.8	31.8	31.7	31.6
34	33.3	33.2	33.1	33.0	33.0	32.9	32.8	32.7	32.7	32.6
35	34.3	34.2	34.1	34.0	34.0	33.9	33.8	33.7	33.6	33.6
36	35.2	35.2	35.1	35.0	34.9	34.9	34.8	34.7	34.6	34.5
37	36.2	36.2	36.1	36.0	35.9	35.8	35.8	35.7	35.6	35.5
38	37.2	37.2	37.1	37.0	36.9	36.8	36.8	36.7	36.6	36.5
39	38.2	38.1	38.1	38.0	37.9	37.8	37.7	37.6	37.6	37.5
40	39.2	39.1	39.0	39.0	38.9	38.8	38.7	38.6	38.5	38.5
41	40.2	40.1	40.0	39.9	39.9	39.8	39.7	39.6	39.5	39.4
42	41.2	41.1	41.0	40.9	40.8	40.8	40.7	40.6	40.5	40.4
43	42.2	42.1	42.0	41.9	41.8	41.7	41.7	41.6	41.5	41.4
44	43.1	43.1	43.0	42.9	42.8	42.7	42.6	42.5	42.5	42.4
45	44.1	44.0	44.0	43.9	43.8	43.7	43.6	43.5	43.4	43.3
46	45.1	45.0	44.9	44.9	44.8	44.7	44.6	44.5	44.4	44.3
47	46.1	46.0	45.9	45.8	45.7	45.7	45.6	45.5	45.4	45.3
48	47.1	47.0	46.9	46.8	46.7	46.6	46.5	46.5	46.4	46.3
49	48.1	48.0	47.9	47.8	47.7	47.6	47.5	47.4	47.4	47.3
50	49.1	49.0	48.9	48.8	48.7	48.6	48.5	48.4	48.3	48.2
51	50.1	50.0	49.9	49.8	49.7	49.6	49.5	49.4	49.3	49.2
52	51.0	50.9	50.8	50.7	50.6	50.5	50.4	50.4	50.3	50.2
53	52.0	51.9	51.8	51.7	51.6	51.5	51.4	51.3	51.2	51.1
54	53.0	52.9	52.8	52.7	52.6	52.5	52.4	52.3	52.2	52.1
55	54.0	53.9	53.8	53.7	53.6	53.5	53.4	53.3	53.2	53.1
56	55.0	54.9	54.8	54.6	54.5	54.4	54.3	54.2	54.1	54.0
57	55.9	55.8	55.7	55.6	55.5	55.4	55.3	55.2	55.1	55.0
58	56.9	56.8	56.7	56.6	56.5	56.4	56.3	56.2	56.1	56.0
59	57.9	57.8	57.7	57.6	57.5	57.4	57.3	57.2	57.1	57.0
60	58.9	58.8	58.7	58.6	58.5	58.3	58.2	58.1	58.0	57.9

Indication	TEMPERATURES									
	80°	81°	82°	83°	84°	85°	86°	87°	88°	89°
15	14.0	14.0	13.9	13.9	13.8	13.8	13.8	13.7	13.7	13.6
16	15.0	15.0	14.9	14.9	14.8	14.8	14.8	14.7	14.7	14.6
17	15.9	15.9	15.8	15.8	15.7	15.7	15.7	15.6	15.6	15.5
18	16.9	16.9	16.8	16.8	16.7	16.7	16.7	16.6	16.6	16.5
19	17.9	17.9	17.8	17.8	17.7	17.7	17.6	17.6	17.5	17.5
20	18.9	18.8	18.7	18.7	18.7	18.6	18.6	18.5	18.5	18.4
21	19.8	19.8	19.7	19.7	19.6	19.6	19.5	19.5	19.4	19.4
22	20.8	20.7	20.7	20.6	20.6	20.5	20.5	20.4	20.4	20.3
23	21.8	21.7	21.6	21.6	21.6	21.5	21.5	21.4	21.3	21.3
24	22.8	22.7	22.6	22.6	22.5	22.5	22.4	22.4	22.3	22.3
25	23.7	23.7	23.6	23.6	23.5	23.5	23.4	23.3	23.3	23.2
26	24.7	24.6	24.6	24.5	24.5	24.4	24.4	24.3	24.2	24.2
27	25.7	25.6	25.5	25.5	25.5	25.4	25.3	25.3	25.2	25.2
28	26.7	26.6	26.5	26.5	26.4	26.4	26.3	26.2	26.2	26.1
29	27.6	27.6	27.5	27.5	27.4	27.3	27.3	27.2	27.1	27.1
30	28.6	28.6	28.5	28.4	28.4	28.3	28.2	28.2	28.1	28.0
31	29.6	29.5	29.5	29.4	29.3	29.3	29.2	29.1	29.1	29.0
32	30.6	30.5	30.4	30.4	30.3	30.2	30.2	30.1	30.0	30.0
33	31.6	31.5	31.4	31.3	31.3	31.2	31.1	31.1	31.0	30.9
34	32.5	32.5	32.4	32.3	32.2	32.2	32.1	32.0	32.0	31.9
35	33.5	33.4	33.3	33.3	33.2	33.1	33.1	33.0	32.9	32.8
36	34.5	34.4	34.3	34.3	34.2	34.1	34.0	34.0	33.9	33.8
37	35.5	35.4	35.3	35.2	35.1	35.1	35.0	34.9	34.8	34.8
38	36.4	36.4	36.3	36.2	36.1	36.0	36.0	35.9	35.8	35.7
39	37.4	37.3	37.2	37.2	37.1	37.0	36.9	36.8	36.8	36.7
40	38.4	38.3	38.2	38.1	38.1	38.0	37.9	37.8	37.7	37.7
41	39.4	39.3	39.2	39.1	39.0	38.9	38.9	38.8	38.7	38.6
42	40.3	40.3	40.2	40.1	40.0	39.9	39.8	39.8	39.7	39.6
43	41.3	41.2	41.2	41.1	41.0	40.9	40.8	40.7	40.6	40.6
44	42.3	42.2	42.1	42.0	42.0	41.9	41.8	41.7	41.6	41.5
45	43.3	43.2	43.1	43.0	42.9	42.8	42.8	42.7	42.6	42.5
46	44.2	44.2	44.1	44.0	43.9	43.8	43.7	43.6	43.6	43.5
47	45.2	45.1	45.0	45.0	44.9	44.8	44.7	44.6	44.5	44.4
48	46.2	46.1	46.0	45.9	45.8	45.7	45.7	45.6	45.5	45.4
49	47.2	47.1	47.0	46.9	46.8	46.7	46.6	46.5	46.5	46.4
50	48.1	48.0	48.0	47.9	47.8	47.7	47.6	47.5	47.4	47.4
51	49.1	49.0	48.9	48.8	48.7	48.6	48.6	48.5	48.4	48.3
52	50.1	50.0	49.9	49.8	49.7	49.6	49.5	49.4	49.4	49.3
53	51.0	50.9	50.9	50.8	50.7	50.6	50.5	50.4	50.3	50.2
54	52.0	51.9	51.8	51.7	51.6	51.5	51.4	51.3	51.3	51.2
55	53.0	52.9	52.8	52.7	52.6	52.5	52.4	52.3	52.2	52.1
56	53.9	53.8	53.7	53.6	53.5	53.4	53.4	53.3	53.2	53.1
57	54.9	54.8	54.7	54.6	54.5	54.4	54.3	54.2	54.1	54.0
58	55.9	55.8	55.7	55.6	55.5	55.4	55.3	55.2	55.1	55.0
59	56.8	56.7	56.6	56.5	56.4	56.3	56.2	56.1	56.0	55.9
60	57.8	57.7	57.6	57.5	57.4	57.3	57.2	57.1	57.0	56.9

## 10 PAINT VEHICLES, JAPANS AND VARNISHES

TABLE II

7. Specific gravity corresponding to degrees Baumé at  $60^{\circ}\text{F. } 15.5^{\circ}\text{C.}$   
 $60^{\circ}\text{F. } 15.5^{\circ}\text{C.}$ 

$$\text{Formula Sp. Gr.} = \frac{141.5}{131.5 + B}$$

## TENTHS OF DEGREES

Degrees Baumé	0	1	2	3	4	5	6	7	8	9
10	1.0000	.9993	.9986	.9979	.9972	.9965	.9958	.9951	.9944	.9937
11	.9930	.9923	.9916	.9909	.9902	.9895	.9888	.9881	.9874	.9868
12	.9861	.9854	.9847	.9840	.9833	.9826	.9820	.9813	.9806	.9799
13	.9792	.9786	.9779	.9772	.9765	.9759	.9752	.9745	.9738	.9732
14	.9725	.9718	.9712	.9705	.9698	.9692	.9685	.9679	.9672	.9665
15	.9659	.9652	.9646	.9639	.9632	.9626	.9619	.9613	.9606	.9600
16	.9593	.9587	.9580	.9574	.9567	.9561	.9554	.9548	.9542	.9535
17	.9529	.9522	.9516	.9509	.9503	.9497	.9490	.9484	.9478	.9471
18	.9465	.9459	.9452	.9446	.9440	.9433	.9427	.9421	.9415	.9408
19	.9402	.9396	.9390	.9383	.9377	.9371	.9365	.9359	.9352	.9346
20	.9340	.9334	.9328	.9322	.9315	.9309	.9303	.9297	.9291	.9285
21	.9279	.9273	.9267	.9260	.9254	.9248	.9242	.9236	.9230	.9224
22	.9218	.9212	.9206	.9200	.9194	.9188	.9182	.9176	.9170	.9165
23	.9159	.9153	.9147	.9141	.9135	.9129	.9123	.9117	.9111	.9106
24	.9100	.9094	.9088	.9082	.9076	.9071	.9065	.9059	.9053	.9047
25	.9042	.9036	.9030	.9024	.9018	.9013	.9007	.9001	.8996	.8990
26	.8984	.8978	.8973	.8967	.8961	.8956	.8950	.8944	.8939	.8933
27	.8927	.8922	.8916	.8911	.8905	.8899	.8894	.8888	.8883	.8877
28	.8871	.8866	.8860	.8855	.8849	.8844	.8838	.8833	.8827	.8822
29	.8816	.8811	.8805	.8800	.8794	.8789	.8783	.8778	.8772	.8767
30	.8762	.8756	.8751	.8745	.8740	.8735	.8729	.8724	.8718	.8713
31	.8708	.8702	.8697	.8692	.8686	.8681	.8676	.8670	.8665	.8660
32	.8654	.8649	.8644	.8639	.8633	.8628	.8623	.8618	.8612	.8607
33	.8602	.8597	.8591	.8586	.8581	.8576	.8571	.8565	.8560	.8555
34	.8550	.8545	.8540	.8534	.8529	.8524	.8519	.8514	.8509	.8504
35	.8498	.8493	.8488	.8483	.8478	.8473	.8468	.8463	.8458	.8453
36	.8448	.8443	.8438	.8433	.8428	.8423	.8418	.8413	.8408	.8403
37	.8398	.8393	.8388	.8383	.8378	.8373	.8368	.8363	.8358	.8353
38	.8348	.8343	.8338	.8333	.8328	.8324	.8319	.8314	.8309	.8304
39	.8299	.8294	.8289	.8285	.8280	.8275	.8270	.8265	.8260	.8256
40	.8251	.8246	.8241	.8236	.8232	.8227	.8222	.8217	.8212	.8208
41	.8203	.8198	.8193	.8189	.8184	.8179	.8174	.8170	.8165	.8160
42	.8156	.8151	.8146	.8142	.8137	.8132	.8128	.8123	.8118	.8114
43	.8109	.8104	.8100	.8095	.8090	.8086	.8081	.8076	.8072	.8067
44	.8063	.8058	.8053	.8049	.8044	.8040	.8035	.8031	.8026	.8022
45	.8017	.8012	.8008	.8003	.7999	.7994	.7990	.7985	.7981	.7976
46	.7972	.7967	.7963	.7958	.7954	.7949	.7945	.7941	.7936	.7932
47	.7927	.7923	.7918	.7914	.7909	.7905	.7901	.7896	.7892	.7887
48	.7883	.7879	.7874	.7870	.7865	.7861	.7857	.7852	.7848	.7844
49	.7839	.7835	.7831	.7826	.7822	.7818	.7813	.7809	.7805	.7800
50	.7796	.7792	.7788	.7783	.7779	.7775	.7770	.7766	.7762	.7758
51	.7753	.7749	.7745	.7741	.7736	.7732	.7728	.7724	.7720	.7715
52	.7711	.7707	.7703	.7699	.7694	.7690	.7686	.7682	.7678	.7674
53	.7669	.7665	.7661	.7657	.7653	.7649	.7645	.7640	.7636	.7632
54	.7628	.7624	.7620	.7616	.7612	.7608	.7603	.7599	.7595	.7591
55	.7587	.7583	.7579	.7575	.7571	.7567	.7563	.7559	.7555	.7551
56	.7547	.7543	.7539	.7535	.7531	.7527	.7523	.7519	.7515	.7511
57	.7507	.7503	.7499	.7495	.7491	.7487	.7483	.7479	.7475	.7471
58	.7467	.7463	.7459	.7455	.7451	.7447	.7443	.7440	.7436	.7432
59	.7428	.7424	.7420	.7416	.7412	.7408	.7405	.7401	.7397	.7393

## TENTHS OF DEGREES

Degrees Baumé	0	1	2	3	4	5	6	7	8	9
60	.7389	.7385	.7381	.7377	.7374	.7370	.7366	.7362	.7358	.7354
61	.7351	.7347	.7343	.7339	.7335	.7332	.7328	.7324	.7320	.7316
62	.7313	.7309	.7305	.7301	.7298	.7294	.7290	.7286	.7283	.7279
63	.7275	.7271	.7268	.7264	.7260	.7256	.7253	.7249	.7245	.7242
64	.7238	.7234	.7230	.7227	.7223	.7219	.7216	.7212	.7208	.7205
65	.7201	.7197	.7194	.7190	.7186	.7183	.7179	.7175	.7172	.7168
66	.7165	.7161	.7157	.7154	.7150	.7146	.7143	.7139	.7136	.7132
67	.7128	.7125	.7121	.7118	.7114	.7111	.7107	.7103	.7100	.7096
68	.7093	.7089	.7086	.7082	.7079	.7075	.7071	.7068	.7064	.7061
69	.7057	.7054	.7050	.7047	.7043	.7040	.7036	.7033	.7029	.7026
70	.7022	.7019	.7015	.7012	.7008	.7005	.7001	.6998	.6995	.6991
71	.6988	.6984	.6981	.6977	.6974	.6970	.6967	.6964	.6960	.6957
72	.6953	.6950	.6946	.6943	.6940	.6936	.6933	.6929	.6926	.6923
73	.6919	.6916	.6912	.6909	.6906	.6902	.6899	.6896	.6892	.6889
74	.6886	.6882	.6879	.6876	.6872	.6869	.6866	.6862	.6859	.6856
75	.6852	.6849	.6846	.6842	.6839	.6836	.6832	.6829	.6826	.6823
76	.6819	.6816	.6813	.6809	.6806	.6803	.6800	.6796	.6793	.6790
77	.6787	.6783	.6780	.6777	.6774	.6770	.6767	.6764	.6761	.6757
78	.6754	.6751	.6748	.6745	.6741	.6738	.6735	.6732	.6728	.6725
79	.6722	.6719	.6716	.6713	.6709	.6706	.6703	.6700	.6697	.6693
80	.6690	.6687	.6684	.6681	.6678	.6675	.6671	.6668	.6665	.6662
81	.6659	.6656	.6653	.6649	.6646	.6643	.6640	.6637	.6634	.6631
82	.6628	.6625	.6621	.6618	.6615	.6612	.6609	.6606	.6603	.6600
83	.6597	.6594	.6591	.6588	.6584	.6581	.6578	.6575	.6572	.6569
84	.6566	.6563	.6560	.6557	.6554	.6551	.6548	.6545	.6542	.6539
85	.6536	.6533	.6530	.6527	.6524	.6521	.6518	.6515	.6512	.6509
86	.6506	.6503	.6500	.6497	.6494	.6491	.6488	.6485	.6482	.6479
87	.6476	.6473	.6470	.6467	.6464	.6461	.6458	.6455	.6452	.6449
88	.6446	.6444	.6441	.6438	.6435	.6432	.6429	.6426	.6423	.6420
89	.6417	.6414	.6411	.6409	.6406	.6403	.6400	.6397	.6394	.6391
90	.6388	.6385	.6382	.6380	.6377	.6374	.6371	.6368	.6365	.6362
91	.6360	.6357	.6354	.6351	.6348	.6345	.6342	.6340	.6337	.6334
92	.6331	.6328	.6325	.6323	.6320	.6317	.6314	.6311	.6309	.6306
93	.6303	.6300	.6297	.6294	.6292	.6289	.6286	.6283	.6281	.6278
94	.6275	.6272	.6269	.6267	.6264	.6261	.6258	.6256	.6253	.6250
95	.6247	.6244	.6242	.6239	.6236	.6233	.6231	.6228	.6225	.6223
96	.6220	.6217	.6214	.6212	.6209	.6206	.6203	.6201	.6198	.6195
97	.6193	.6190	.6187	.6184	.6182	.6179	.6176	.6174	.6171	.6168
98	.6166	.6163	.6160	.6158	.6155	.6152	.6150	.6147	.6144	.6141
99	.6139	.6136	.6134	.6131	.6128	.6126	.6123	.6120	.6118	.6115



TABLE IIa

## 8. Equivalent pounds per gallon to degrees Baumé at 60° F.

## TENTHS OF DEGREES

Degrees Baumé	0	1	2	3	4	5	6	7	8	9
10	8.331	8.325	8.319	8.314	8.308	8.302	8.296	8.290	8.284	8.279
11	8.273	8.267	8.261	8.255	8.249	8.244	8.238	8.232	8.226	8.221
12	8.215	8.209	8.204	8.198	8.192	8.186	8.181	8.175	8.169	8.164
13	8.158	8.153	8.147	8.141	8.135	6.130	8.124	8.119	8.113	8.108
14	8.102	8.096	8.091	8.085	8.079	8.074	8.069	8.064	8.058	8.052
15	8.047	8.041	8.036	8.030	8.024	8.019	8.014	8.009	8.003	7.998
16	7.992	7.987	7.981	7.976	7.970	7.965	7.959	7.954	7.949	7.944
17	7.939	7.933	7.928	7.922	7.917	7.912	7.906	7.901	7.896	7.890
18	7.885	7.880	7.874	7.869	7.864	7.859	7.854	7.849	7.844	7.838
19	7.833	7.828	7.823	7.817	7.812	7.807	7.802	7.797	7.791	7.786
20	7.781	7.776	7.771	7.766	7.760	7.755	7.750	7.745	7.740	7.735
21	7.730	7.725	7.720	7.715	7.710	7.705	7.700	7.695	7.690	7.685
22	7.680	7.675	7.670	7.665	7.660	7.655	7.650	7.645	7.640	7.635
23	7.630	7.625	7.620	7.615	7.610	7.605	7.600	7.595	7.590	7.586
24	7.581	7.576	7.571	7.566	7.561	7.557	7.552	7.547	7.542	7.537
25	7.533	7.528	7.523	7.518	7.513	7.509	7.504	7.499	7.495	7.490
26	7.485	7.480	7.475	7.471	7.465	7.461	7.456	7.451	7.447	7.442
27	7.437	7.433	7.428	7.424	7.419	7.414	7.410	7.405	7.400	7.395
28	7.390	7.386	7.381	7.377	7.372	7.368	7.363	7.359	7.354	7.350
29	7.345	7.340	7.335	7.331	7.326	7.322	7.318	7.313	7.308	7.304
30	7.300	7.295	7.290	7.285	7.281	7.277	7.272	7.268	7.263	7.259
31	7.255	7.250	7.245	7.241	7.236	7.232	7.228	7.223	7.219	7.215
32	7.210	7.205	7.201	7.197	7.192	7.188	7.184	7.180	7.175	7.170
33	7.166	7.162	7.157	7.153	7.149	7.145	7.141	7.136	7.131	7.127
34	7.123	7.119	7.115	7.110	7.106	7.101	7.097	7.093	7.089	7.085
35	7.080	7.076	7.071	7.067	7.063	7.059	7.055	7.051	7.046	7.042
36	7.038	7.034	7.030	7.026	7.021	7.017	7.013	7.009	7.005	7.001
37	6.996	6.992	6.988	6.984	6.980	6.976	6.971	6.967	6.963	6.959
38	6.955	6.951	6.946	6.942	6.938	6.935	6.931	6.926	6.922	6.918
39	6.914	6.910	6.906	6.902	6.898	6.894	6.890	6.886	6.881	6.878
40	6.874	6.870	6.866	6.861	6.858	6.854	6.850	6.846	6.841	6.838
41	6.834	6.830	6.826	6.822	6.818	6.814	6.810	6.806	6.802	6.798
42	6.795	6.791	6.786	6.783	6.779	6.775	6.771	6.767	6.763	6.760
43	6.756	6.751	6.748	6.744	6.740	6.736	6.732	6.728	6.725	6.721
44	6.717	6.713	6.709	6.706	6.701	6.698	6.694	6.691	6.686	6.683
45	6.679	6.675	6.671	6.667	6.664	6.660	6.656	6.652	6.649	6.645
46	6.641	6.637	6.634	6.630	6.626	6.623	6.619	6.616	6.611	6.608
47	6.604	6.601	6.596	6.593	6.589	6.586	6.582	6.578	6.575	6.571
48	6.567	6.564	6.560	6.556	6.552	6.549	6.546	6.542	6.538	6.535
49	6.531	6.527	6.524	6.520	6.517	6.513	6.509	6.506	6.502	6.498
50	6.495	6.492	6.488	6.484	6.481	6.477	6.473	6.470	6.467	6.463
51	6.459	6.456	6.452	6.449	6.445	6.442	6.438	6.435	6.432	6.427
52	6.424	6.421	6.417	6.414	6.410	6.407	6.403	6.400	6.397	6.393
53	6.389	6.386	6.382	6.379	6.376	6.372	6.369	6.365	6.362	6.358
54	6.355	6.352	6.348	6.345	6.342	6.338	6.334	6.331	6.327	6.324
55	6.321	6.317	6.314	6.311	6.307	6.304	6.301	6.297	6.294	6.291
56	6.287	6.284	6.281	6.277	6.274	6.271	6.267	6.264	6.261	6.257
57	6.254	6.251	6.247	6.244	6.241	6.237	6.234	6.231	6.227	6.224
58	6.221	6.217	6.214	6.211	6.207	6.204	6.201	6.198	6.195	6.191
59	6.188	6.185	6.182	6.178	6.175	6.172	6.169	6.166	6.162	6.159

TENTHS OF DEGREES

Degrees Baumé	0	1	2	3	4	5	6	7	8	9
60	6.156	6.152	6.149	6.146	6.143	6.140	6.137	6.133	6.130	6.127
61	6.124	6.121	6.117	6.114	6.111	6.108	6.105	6.102	6.098	6.095
62	6.092	6.089	6.086	6.082	6.080	6.077	6.073	6.070	6.067	6.064
63	6.061	6.057	6.055	6.052	6.048	6.045	6.042	6.039	6.036	6.033
64	6.030	6.027	6.023	6.021	6.017	6.014	6.012	6.008	6.005	6.002
65	5.999	5.996	5.993	5.990	5.987	5.984	5.981	5.977	5.975	5.972
66	5.969	5.966	5.962	5.960	5.957	5.953	5.951	5.948	5.945	5.942
67	5.938	5.936	5.933	5.930	5.927	5.924	5.921	5.918	5.915	5.912
68	5.909	5.906	5.903	5.900	5.898	5.894	5.891	5.888	5.885	5.883
69	5.879	5.877	5.873	5.871	5.868	5.865	5.862	5.859	5.856	5.853
70	5.850	5.848	5.844	5.842	5.838	5.836	5.833	5.830	5.828	5.824
71	5.822	5.818	5.816	5.813	5.810	5.807	5.804	5.802	5.798	5.796
72	5.793	5.790	5.787	5.784	5.782	5.778	5.776	5.773	5.770	5.768
73	5.764	5.762	5.758	5.756	5.753	5.750	5.748	5.745	5.742	5.739
74	5.737	5.733	5.731	5.728	5.725	5.723	5.720	5.717	5.714	5.712
75	5.708	5.706	5.703	5.700	5.698	5.695	5.692	5.689	5.687	5.684
76	5.681	5.678	5.676	5.673	5.670	5.668	5.665	5.662	5.659	5.657
77	5.654	5.651	5.648	5.646	5.643	5.640	5.638	5.635	5.633	5.629
78	5.627	5.624	5.622	5.619	5.616	5.613	5.611	5.608	5.605	5.603
79	5.600	5.597	5.595	5.593	5.589	5.587	5.584	5.582	5.579	5.576
80	5.573	5.571	5.568	5.566	5.563	5.561	5.558	5.555	5.553	5.550
81	5.548	5.545	5.543	5.540	5.537	5.534	5.532	5.529	5.527	5.524
82	5.522	5.519	5.516	5.513	5.511	5.508	5.506	5.503	5.501	5.498
83	5.496	5.493	5.491	5.488	5.485	5.483	5.480	5.478	5.475	5.473
84	5.470	5.468	5.465	5.463	5.460	5.458	5.455	5.453	5.450	5.448
85	5.445	5.443	5.440	5.438	5.435	5.433	5.430	5.428	5.425	5.423
86	5.420	5.418	5.415	5.413	5.410	5.408	5.405	5.403	5.400	5.398
87	5.395	5.393	5.390	5.388	5.385	5.383	5.380	5.378	5.375	5.373
88	5.370	5.368	5.366	5.363	5.361	5.358	5.356	5.353	5.351	5.349
89	5.346	5.344	5.341	5.339	5.337	5.334	5.332	5.329	5.327	5.324
90	5.322	5.319	5.317	5.315	5.313	5.310	5.308	5.305	5.303	5.300
91	5.299	5.296	5.294	5.291	5.289	5.286	5.284	5.282	5.279	5.277
92	5.274	5.272	5.269	5.268	5.265	5.263	5.260	5.258	5.256	5.254
93	5.251	5.249	5.246	5.244	5.242	5.239	5.237	5.234	5.233	5.230
94	5.228	5.225	5.223	5.221	5.219	5.216	5.214	5.212	5.209	5.207
95	5.204	5.202	5.200	5.198	5.195	5.193	5.191	5.189	5.186	5.184
96	5.182	5.179	5.177	5.175	5.173	5.170	5.168	5.166	5.164	5.161
97	5.159	5.157	5.154	5.152	5.150	5.148	5.145	5.144	5.141	5.139
98	5.137	5.134	5.132	5.130	5.128	5.125	5.124	5.121	5.119	5.116
99	5.114	5.112	5.110	5.108	5.105	5.104	5.101	5.099	5.097	5.094

## CHAPTER II

### EXAMINATION OF PETROLEUM THINNERS (Continued)

**9. Composition.** In the distillation of petroleum thinners, one has to deal with a solvent composed of a large number of compounds or series of compounds, the members of which so closely resemble each other in their physical and chemical properties that absolute differentiation by any simple means is very difficult and practically impossible. Distillation is the simplest method of securing an approximate separation.

The success of this method depends chiefly on a close adjustment and control of the distilling temperature.

**10. Difficulties encountered in the ordinary methods.** The use of the Engler distilling flask heated with a Bunsen flame is too well known to need description here, but connected with its use are many difficulties that are often not appreciated. The continual wavering of the flame, even when carefully screened from air currents, the fluctuation of the gas pressure, and the condensation of the vapors in the neck of the flask which cause them to "crack" or become partially decomposed when dropping on the hot liquid below, cause irregularity in the rate of distillation. Duplication of results, whether by the same operator or others, does not, therefore, yield fractions that are alike either in quantity or quality. The same is true when the Engler flask is immersed in an oil bath, though not to such a great extent.

Experience has taught the author that petroleum thinners, as produced at the present time, do not run sufficiently uniform to be satisfactory at all times in the manufacture of the highly specialized enamels, paints, and varnishes used in the various manufacturing industries.

The ordinary methods of distillation having proven inadequate for the correct valuation of such thinners, the author began a search for a more careful and suitable means of procedure. The apparatus here described has proven very satisfactory and is the method used in the Petroleum Laboratory of the Bureau of Mines.<sup>1</sup>

**11. Apparatus used.** The apparatus consists essentially of two pear-shaped halves of heat-resisting material inclosing and closely fitting a standard Engler flask. The halves have imbedded on their inner surface a metal-resistance wire wound back and forth for conducting an electric current which is the heating element. The heated wire warms the flask and contents, causing the distillation to proceed quietly and uniformly. Very close duplicates can be obtained by this method.

**12. Construction of the heater.** The body of the heater is composed of 100 parts by weight of powdered magnesia, 100 parts of powdered silica, 40 parts of shredded asbestos, and 10 parts freely soluble powdered sodium silicate, or a solution of 40° Bé. water glass, containing an equivalent quantity of sodium silicate. The above components are first thoroughly mixed and then made into a paste with a 10 per cent solution of magnesium chloride.

<sup>1</sup> Original Communications, Eighth International Congress of Applied Chemistry, Section IV, page 15.



The form for the mold is made by turning from a block of soft pine a model having the same size and form as that of the standard Engler flask, described below, the bulb and neck being turned in one piece. Saw the model into halves from top to bottom. Hollow out the neck and bulb to form a shallow dipper, making the cavity about 1 cm. deep and leaving the rim about 3 mm. thick. Drill holes the size of small wire brads 1 cm. apart and 3 mm. below the edge of the rim of the dipper and along the neck. Insert brads or small nails from the inside through the holes, allowing the points to project about 3 mm., as shown in Fig. 1.

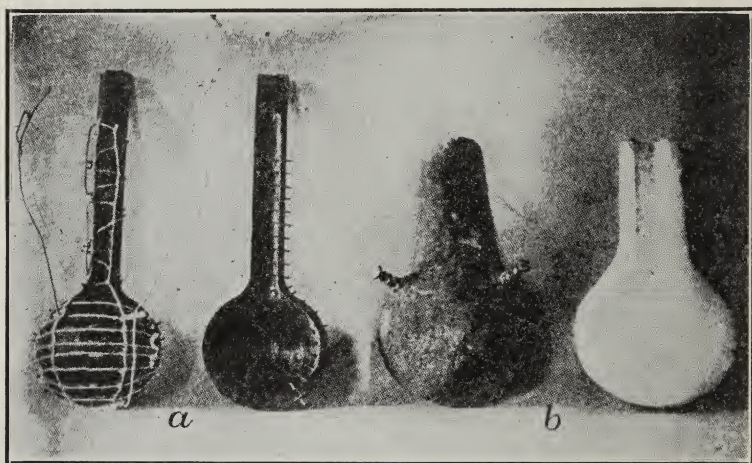


FIG. 1. — CONSTRUCTION OF HEATER

A standard Engler flask of the capacity and dimensions specified in Fig. 2 should be used in designing the model, and particular emphasis should be used in specifying these flasks when ordering from the supply house, as the so-called Engler flasks, listed in most catalogues, vary widely from the specified dimensions.

**13. Wiring.** Any high-resistance wire can be used, but a No. 24 nickel-chromium wire gives the most satisfactory results. The manner of wiring the halves of the heater is of prime importance. Winding the wires equidistant from one another from the bottom of the flask to the top of the neck develops too great

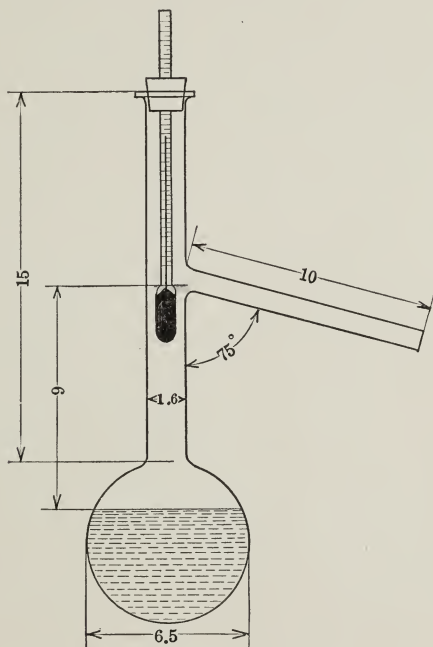


FIG. 2.— ENGLER FLASK

a heat in the neck, thus superheating the vapors, causing them to “crack.” Leaving the neck entirely unwound causes the vapors to condense, resulting in partial decomposition or cracking of the thinner. The manner of wiring shown in Fig. 1 gives a fairly uniform temperature from the bottom of the flask to the side arm where the vapors are given off. In the case of the unprotected Engler flask, where there is direct

heating by the flame or where the flask is immersed in an oil bath, the temperature of the vapors at the side arm may be from 20–40° C. cooler than the temperature of the boiling liquid.

The method of winding used by the author has 11 cross wires on the bulb, 5 cross wires on the neck below the side arm, and 4 cross wires on the neck above the side arm, making a total of 20 wires on each half of the heater. The relation of wiring to the temperature at the different parts of the flask can readily be ascertained by placing thermometers at different levels during the distillation of a liquid of constant boiling point.

After greasing the convex surface of the mold to prevent the paste from sticking to it, wind the resistance wire back and forth as shown in Fig. 1, tying the wire in place with asbestos cord and fastening the ends of the wire to binding posts projecting at convenient positions. Lay the wired mold, convex side up, on a smooth surface covered with a sheet of paper and apply the freshly prepared paste to the desired thickness, usually about one-half inch.

**14. Drying.** After allowing the paste to set, preferably over night in a cool place, remove the brads from the inside of the mold and carefully loosen the mold from the shell thus formed. The heater is then dried in an oven at 50° C. for about 24 hours, after which it is slowly heated up to 200° C. to remove the last traces of moisture. The drying must be carefully carried out so as to prevent cracking and warping. The completed half of the heater is shown in Fig. 1 b.

**15. Temperature control.** The temperature being controlled by the current, it is necessary to have some



form of rheostat. The cheapest type having the greatest range of resistance is the water rheostat. The one used by the author is constructed as follows: An ordinary three-gallon stone jar is filled with a very dilute solution of sulphuric acid. The electrodes are of sheet lead, one being in the shape of an "L," which is stationary, the other triangular and suspended from a windlass which is provided with a brake.

The two halves of the heater, the rheostat and an ammeter, are connected in series with the lighting circuit (see Fig. 3). The current and consequently the

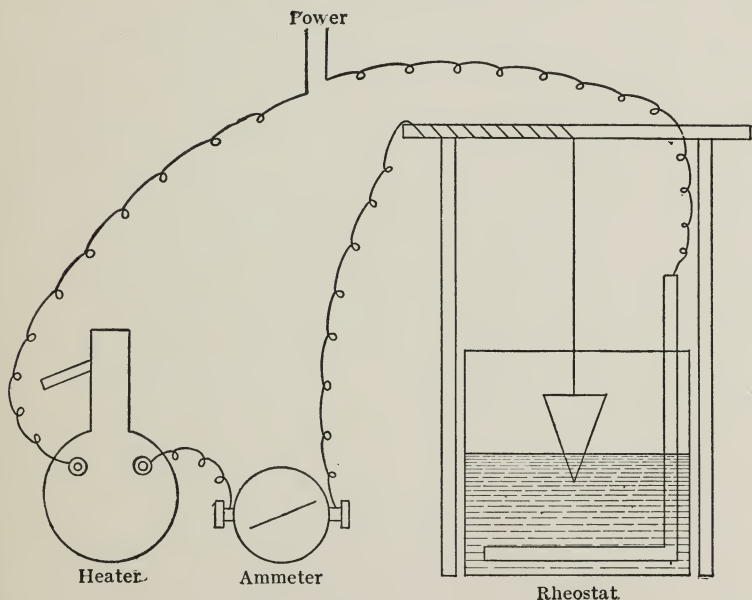


FIG. 3

temperature is controlled by lowering or raising the triangular electrode. The range of current for most thinners is from 2 amps. at the beginning to 3.5–4.0 amps. at the end of the distillation.

The heater should be given a thorough test before being accepted as satisfactory. It may be necessary to make changes in the manner of wiring such as changing the number of turns of wire on the neck. It is essential to have the temperature of the vapors at the neck in close agreement with the temperature of the boiling liquid. There should not be a difference of over three degrees Centigrade between the vapors and the boiling liquid. The rate of distillation should be about 1 c.c. per minute. This is best observed by using two or more thermometers during the trial test while the distillation proceeds as previously described.

**16. Bumping.** The tendency of the liquid to bump in an electrically heated flask is greater than when the flask is heated by a gas flame. This is best prevented by using a fresh boiling stone such as a piece of pumice with each distillation.

*Standard Method of Distillation Adopted by American Society for Testing Materials (1917)*

**17. Apparatus.** The general arrangement of the apparatus is shown in Fig. 4.

**18. Flask.** The flask used shall be the Standard Engler flask, as described in the various standard works upon petroleum, such as Redwood, Holde, etc.

"Engler employs a globular flask 6.5 cm. in diameter, with a cylindrical neck 1.6 cm. in internal diameter and 15 cm. in length, from the side of which a vapor tube 10 cm. in length extends at an angle of 75 degrees downwards to the condenser. The junction of the vapor tube with the neck of the flask should be 9 cm. above the surface of the oil when the flask contains its charge of 100 c.c. of oil. The observance of

the prescribed dimensions is considered essential to the attainment of uniformity of results.”<sup>1</sup>

The flask shall be supported in a ring of asbestos having an opening  $1\frac{1}{4}$  in. in diameter in its center.

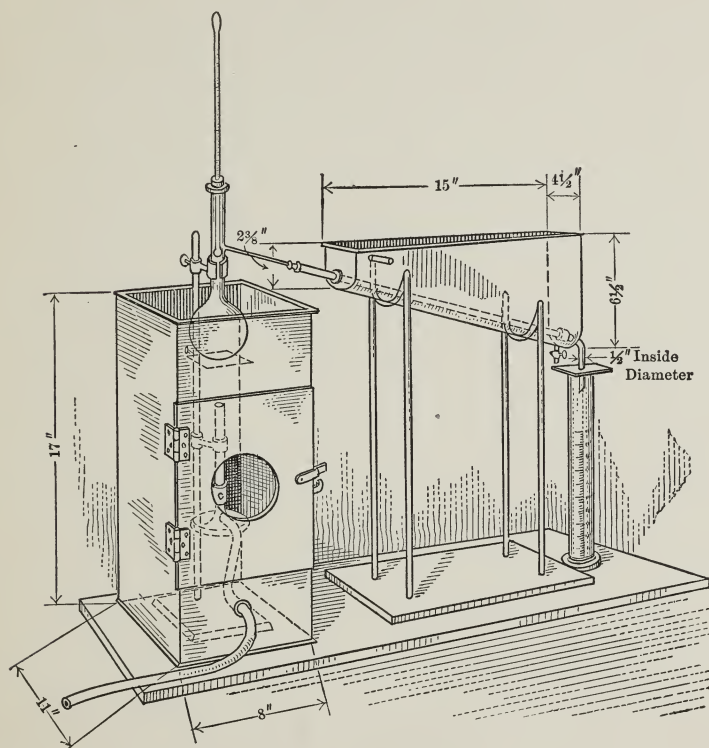


FIG. 4. — DISTILLATION APPARATUS

The flask, burner, etc., shall be surrounded by a shield.

**19. Condenser.** The condenser shall consist of a tube of thin brass of  $\frac{1}{2}$  in. internal diameter, 22 in. in length, set at an angle of 75 degrees with the flask and surrounded by a water jacket of the trough type.

<sup>1</sup> Redwood, 3d edition, Vol. 2, page 205 (1913).

The lower end of the condenser shall be cut off at an acute angle and shall be curved down for a length of 3 in., so as to project at least  $\frac{1}{2}$  in. into the 100-c.c. cylinder used as a receiver.

A cover (pasteboard) should be placed over the top of the cylinder and surrounding the condenser tube.

**20. Thermometer.** The thermometer used shall conform to the following specifications:

The thermometer shall be graduated from 0 to 400° C. in intervals of 1° C. There shall be a small reservoir above the 400° mark. The thermometer shall be finished at the top with a small glass ring. The stem shall be made of enamel-backed thermometer tubing, but not of Jena 16<sup>III</sup> glass. The bulb shall be made of Jena 16<sup>III</sup>, Corning normal, or Jena or Corning borosilicate glass.

Every fifth graduation shall be longer than the intermediate ones, and the marks shall be numbered at every interval of 10°. The graduation marks shall be clear-cut and fine, and the numbering clear-cut and distinct. The thermometer shall be filled above the mercury with an inert gas which will not act chemically or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale, but the upper reservoir shall be large enough so that the pressure will not become excessive at the highest temperature.

The thermometer shall be thoroughly annealed before the final filling. It shall be pointed for use at full immersion.

Each thermometer shall be provided with a suitable case. A serial number for identification and the word "Distillation" shall be engraved on the stem.

All material and workmanship shall be of the best grade.

The maximum error of 0° to 200° C. shall not exceed 0° .5 C.; from 200° to 300° C., shall not exceed 1° C.; and from 300° to 400° C., shall not exceed 2° C.

The thermometer shall conform to the following dimensions:

Total length, max., mm.....	385
Diameter of stem, mm.....	5.5-7.0
Diameter of bulb, mm.....	5.5-7.0
Diameter of capillary, min., mm.....	0.1
Length of bulb, mm.....	11-15
Distance, 0° to bottom of bulb, mm.....	25-35
Distance, 0° to 400° mark, mm.....	280-300

The thermometer shall be inserted through a tight-fitting cork in the neck of the flask, so that the top of the thermometer bulb will be on a level with the bottom of the side outlet in the neck of the flask and in the center of the neck.

**21. Method of distillation.** The flask, connected with the condenser, shall be filled with 100 c.c. of the thinner at 60° F., which shall be measured in the 100-c.c. receiving cylinder. The same cylinder may be used without drying as the receiving vessel for the distillate. The flask shall be heated directly by a suitable burner.

The distillation shall proceed at the rate of not less than 4 or more than 5 c.c. per minute into the receiving cylinder. The temperature at which the first drop leaves the lower end of the condenser shall be considered the initial boiling point.

Readings of the quantity in the receiver shall be taken when the next 10° point is reached, and for every even 10° thereafter. For example, if initial boiling point occurs at 144° C., then the first reading of the

*Handwritten:*  
 suggested  
 distillation  
 T-8

*Handwritten:*  
 Boiling Point  
 T-12



quantity in the receiver shall be made at  $150^{\circ}\text{C}.$ , and thereafter at  $160^{\circ}$ ,  $170^{\circ}$ , etc.

The distillation shall be continued until the point is reached where the last drop is vaporized, when a puff of white vapor usually appears in the bottom of the flask. The temperature at this point shall be considered the end or dry point of distillation.

The total yield of distillate shall not be less than 97 per cent.

*Flash point*  
T-18

**22. Flash point.** In the various methods now in use for the determination of the flash point of an oil, the temperature at which it flashes is not a definite factor but is dependent on chemical and physical conditions over which the operator has no control. It is an indication only of the temperature at which the oil vapors are given off in such quantities as to form an inflammable mixture with air, and is not necessarily a factor influencing the value of an oil for a particular purpose. In the paint and varnish industries, however, it is an important factor, inasmuch as thinners of too low a flash point are undesirable on account of fire risk.

Factors to be considered in making the determination: In taking the flash point, a fresh sample should always be used. The conditions of the test should be as near to those found in practice as is possible. The oil should not be allowed to stand in the cup too long before the flash point is taken, as the lighter portions of the volatile oils will be given off, thus raising the flash point. Barometric pressure influences the flash point to a large degree. A rise of 1 mm. in the barometric pressure changes the flash point on an average of  $0.0381^{\circ}\text{C}.$  The barometric pressure should be taken at the same time as flash points are made, and the correction made.

**23. Shape.** The shape and size of the cup are important. The greater the area exposed, the more rapid will be the evolution of the lighter vapors and the easier it will be to obtain an inflammable mixture, thus lowering the flash point. The cup should always be filled to the mark with *cold* oil and the warming applied very cautiously. The expansion of the oil above the mark due to the warming is generally disregarded. The rate of heating should be such as to keep equilibrium between the liquid and gaseous phases with the temperature rising not over  $3^{\circ}\text{C.}$  per minute. The heating should begin at least  $10^{\circ}\text{C.}$  below the flash point in order that the proper equilibrium may be reached at the point where the oil flashes. This must be determined by a preliminary test.

**24. Stirring.** It is necessary to stir the oil when making a flash point determination, as the temperature of the oil in different parts of the cup may vary from  $3^{\circ}$ – $5^{\circ}\text{C.}$  or even more.

**25. Flame.** A test flame, the size of the ivory bead on the cover of the Abel-Pensky tester, burns about 0.1 cu. ft. of coal gas per hour. A test flame of half this size raises the flash point  $1^{\circ}$  and a flame one and a half times the size of the bead lowers the flash point  $0.5^{\circ}$ .

It is important that the test flame be kept a constant distance from the surface of the oil. If the flame is too near the oil, local heating will result, thus causing the flash point to be lowered. Conversely, if the flame is too far away from the oil, it will take longer for the vapors to be given off in sufficient quantities to flash and the flash point will be higher. A coal gas flame gives a flash point  $0.3^{\circ}$  lower than

does an oil test flame. The electric spark gives a variable but usually a lower result. On account of the variable intensity and duration, the results are bound to be uncertain and should not be used, therefore, with an official instrument. The duration of the exposure of the test flame to the oil vapors is important, chiefly, on account of local heating.

**26. The Abel-Pensky tester and U. S. Bureau of Mines Flash Tester.** The tester most widely used and which satisfactorily meets the required conditions is the closed Abel-Pensky tester, with stirrer, overflow cup, water or oil bath and mechanical exposure of the test flame for exactly one second, and fitted with standardized thermometers. It is the official instrument in Austria-Hungary, Belgium, Denmark, France, Germany, Great Britain, Holland, Italy, Japan, Norway, Roumania, Russia, and Sweden.

The U. S. Bureau of Mines Flash Tester was designed by the Bureau of Mines after having made an exhaustive study of the subject from previously obtained data and actual tests. It has the following advantages over other types: It most nearly reproduces the actual working conditions under which oils are used; it is entirely mechanical in operation, thereby eliminating the personal error in the making of the test; it gives results that are reproduceable by another operator and are directly comparable with those of the standard instruments used by all the leading European and Asiatic countries.

**27. War Department specifications for mineral spirits.** This shall be a hydrocarbon distillate, water white, neutral, clear and free from water. It shall have no darkening effect when mixed with basic carbonate white lead.



When 10 c.c. are put in a glass crystallizing dish  $2\frac{1}{2}$  inches in diameter, and placed on a steam bath for  $2\frac{1}{2}$  hours, the residue must not exceed .03 gms.

When tested according to the standard tests for paint thinners other than turpentine, prescribed by the American Society for Testing Materials, the flash point shall not be less than  $29^{\circ}\text{C}$ . ( $85^{\circ}\text{F}$ .) in a closed tester, and in the distillation test the first drop must issue from the condenser at a temperature not below  $129^{\circ}\text{C}$ . ( $265^{\circ}\text{F}$ .), and 97 per cent must distill below  $243^{\circ}\text{C}$ . ( $470^{\circ}\text{F}$ .). Adopted May 7, 1918.

## CHAPTER III

### EXAMINATION OF TURPENTINE

**28. Classification of turpentine.** Turpentine distilled from the oleoresin of the pine is known to the trade as gum turpentine or spirits of turpentine, while turpentine obtained from resinous wood is known as wood turpentine. Wood turpentine may be extracted with volatile solvents, by steam or by destructive distillation. Manufacturers of wood turpentine now produce a product that comes within the accepted physical and chemical limits of gum turpentine. The specifications should, therefore, be the same for both. The purchaser should, however, state whether the gum or the wood turpentine is desired.

**29. Specifications.** The following specifications and methods of analysis, except for the flash point and odor, are those proposed by the American Society for Testing Materials.<sup>1</sup>

**30. General appearance.** The turpentine should be clear and free from suspended matter and water.

**31. Odor.** Gum turpentine should have a sweet, pleasing odor and not a woody smell. Wood turpentine should not have a pungent, smoky or offensive creosote odor. In fact, the odor should not be any stronger or more penetrating than that of gum spirits, though it may be quite different in character.

<sup>1</sup> Proceedings of the American Society for Testing Materials, Vol. XIV, Part 1, page 342, and Vol. XV, 1915, Part 1, page 265.

**32. Color.** The color shall be "Standard" when a layer 50 mm. in depth is as light or lighter than a No. 1 Yellow Lovibond glass.

**33. Flash point.** If it is necessary to determine the flash point, the determination may be made as described in the preceding chapter.

**34. Specific gravity.** The specific gravity should not be less than 0.862 or more than 0.872 at 15.5° C.

The determination may be made at room temperature, using the Tagliabue hydrometer for turpentine, graduated in .001 divisions, having a range from 0.830 to 0.890. The temperature of the turpentine should be carefully taken and corrected to 15.5° C. by means of Table III, or by using the coefficient of thermal expansion factor, 0.00082, for each degree Centigrade that the temperature at which the determination was made differs from 15° C.

**35. Refractive index.** The refractive index shall not be less than 1.468 or more than 1.478 at 15.5° C. The determination is made at any convenient temperature with an accurate instrument and the results calculated to 15.5° C., using the factor .00045 for each degree that the temperature of determination differs from 15.5° C.

**36. Distillation.** The initial boiling point shall not be less than 150° C. and not more than 160° C. Ninety per cent of the turpentine shall distill below 170° C.

The distillation should be made with an Engler flask and condenser. The heating is done by placing the flask in a glycerine or oil bath of the general type described in bulletin No. 135 of the Bureau of Chemistry, Department of Agriculture. Fit the flask with a thermometer, reading from 145° C. to 200° C., in such a way that the mercury bulb will be opposite the

TABLE III \*

37. Density of turpentine at temperatures from 10° to 40° C. from its density at 20° C.

°C	0.8631	0.8641	0.8651	0.8661	0.8671	0.8681	0.8691	0.8701	0.8711	0.8722	0.8732	0.8742	0.8752	0.8762	0.8772	0.8782
10	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633	0.8633
11	0.8623	0.8633	0.8643	0.8653	0.8663	0.8673	0.8683	0.8693	0.8703	0.8713	0.8724	0.8734	0.8744	0.8754	0.8764	0.8774
12	0.8614	0.8625	0.8635	0.8645	0.8655	0.8665	0.8675	0.8685	0.8695	0.8705	0.8715	0.8725	0.8735	0.8745	0.8755	0.8765
13	0.8606	0.8616	0.8627	0.8637	0.8647	0.8657	0.8667	0.8677	0.8687	0.8697	0.8707	0.8717	0.8727	0.8737	0.8747	0.8758
14	0.8598	0.8608	0.8618	0.8629	0.8639	0.8649	0.8659	0.8669	0.8679	0.8689	0.8699	0.8709	0.8719	0.8729	0.8739	0.8749
15	0.8590	0.8600	0.8610	0.8620	0.8630	0.8641	0.8651	0.8661	0.8671	0.8681	0.8691	0.8701	0.8711	0.8721	0.8731	0.8741
16	0.8582	0.8592	0.8602	0.8612	0.8622	0.8632	0.8642	0.8652	0.8663	0.8673	0.8683	0.8693	0.8703	0.8713	0.8723	0.8733
17	0.8574	0.8584	0.8594	0.8604	0.8614	0.8624	0.8634	0.8644	0.8654	0.8664	0.8674	0.8684	0.8695	0.8705	0.8715	0.8725
18	0.8566	0.8576	0.8586	0.8596	0.8606	0.8616	0.8626	0.8636	0.8646	0.8656	0.8666	0.8676	0.8686	0.8696	0.8706	0.8716
19	0.8558	0.8568	0.8578	0.8588	0.8598	0.8608	0.8618	0.8628	0.8638	0.8648	0.8658	0.8668	0.8678	0.8688	0.8698	0.8708
20	0.8550	0.8560	0.8570	0.8580	0.8590	0.8600	0.8610	0.8620	0.8630	0.8640	0.8650	0.8660	0.8670	0.8680	0.8690	0.8700
21	0.8542	0.8552	0.8562	0.8572	0.8582	0.8592	0.8602	0.8612	0.8622	0.8632	0.8642	0.8652	0.8662	0.8672	0.8682	0.8692
22	0.8534	0.8544	0.8554	0.8564	0.8574	0.8584	0.8594	0.8604	0.8614	0.8624	0.8634	0.8644	0.8654	0.8664	0.8674	0.8684
23	0.8526	0.8536	0.8546	0.8556	0.8566	0.8576	0.8586	0.8596	0.8606	0.8616	0.8626	0.8636	0.8646	0.8656	0.8665	0.8675
24	0.8518	0.8528	0.8538	0.8548	0.8558	0.8568	0.8578	0.8587	0.8597	0.8607	0.8617	0.8627	0.8637	0.8647	0.8657	0.8667
25	0.8510	0.8520	0.8530	0.8540	0.8549	0.8559	0.8569	0.8579	0.8589	0.8599	0.8609	0.8619	0.8629	0.8639	0.8649	0.8659
26	0.8502	0.8512	0.8521	0.8531	0.8541	0.8551	0.8561	0.8571	0.8581	0.8591	0.8601	0.8611	0.8621	0.8631	0.8641	0.8651
27	0.8493	0.8503	0.8513	0.8523	0.8533	0.8543	0.8553	0.8563	0.8573	0.8583	0.8593	0.8603	0.8613	0.8623	0.8632	0.8642
28	0.8485	0.8495	0.8505	0.8515	0.8525	0.8535	0.8545	0.8555	0.8565	0.8575	0.8585	0.8594	0.8604	0.8614	0.8624	0.8634
29	0.8477	0.8487	0.8497	0.8507	0.8517	0.8527	0.8537	0.8547	0.8557	0.8566	0.8576	0.8586	0.8596	0.8606	0.8616	0.8626
30	0.8469	0.8479	0.8489	0.8499	0.8509	0.8519	0.8529	0.8538	0.8548	0.8558	0.8568	0.8578	0.8588	0.8598	0.8608	0.8618
31	0.8461	0.8471	0.8481	0.8491	0.8501	0.8510	0.8520	0.8530	0.8540	0.8550	0.8560	0.8570	0.8580	0.8590	0.8600	0.8610
32	0.8453	0.8463	0.8473	0.8483	0.8492	0.8502	0.8512	0.8522	0.8532	0.8542	0.8552	0.8562	0.8572	0.8582	0.8591	0.8601
33	0.8445	0.8455	0.8465	0.8474	0.8484	0.8494	0.8504	0.8514	0.8524	0.8534	0.8544	0.8554	0.8563	0.8573	0.8583	0.8593
34	0.8437	0.8447	0.8456	0.8466	0.8476	0.8486	0.8496	0.8506	0.8516	0.8526	0.8535	0.8545	0.8555	0.8565	0.8575	0.8585
35	0.8429	0.8438	0.8448	0.8458	0.8468	0.8478	0.8488	0.8498	0.8508	0.8517	0.8527	0.8537	0.8547	0.8557	0.8567	0.8576
36	0.8421	0.8430	0.8440	0.8450	0.8460	0.8470	0.8480	0.8490	0.8499	0.8509	0.8519	0.8529	0.8539	0.8549	0.8558	0.8568
37	0.8412	0.8422	0.8432	0.8442	0.8452	0.8462	0.8472	0.8481	0.8491	0.8501	0.8511	0.8521	0.8530	0.8540	0.8550	0.8560
38	0.8404	0.8414	0.8424	0.8434	0.8444	0.8454	0.8463	0.8473	0.8483	0.8493	0.8503	0.8512	0.8522	0.8532	0.8542	0.8552
39	0.8396	0.8406	0.8416	0.8426	0.8435	0.8445	0.8455	0.8465	0.8475	0.8485	0.8494	0.8504	0.8514	0.8524	0.8534	0.8544
40	0.8388	0.8398	0.8408	0.8418	0.8427	0.8437	0.8447	0.8457	0.8467	0.8476	0.8486	0.8496	0.8506	0.8516	0.8526	0.8535

\* Technologic Paper No. 9 Bureau of Standards.

side arm and the 175° mark below the cork. Place 100 c.c. of the turpentine to be examined in the flask, connect with the condenser, insert the stopper bearing the thermometer and heat until the distillation begins. Conduct the distillation so that the distillate passes over at the rate of two drops per second. Note the initial distilling temperature and the percentage distilling below 170° C.

**38. Polymerization.** The polymerization residue shall not exceed 2 per cent, and its refractive index shall not be less than 1.500 at 15.5° C.

Place 20 c.c. of exactly 38 times normal (100.92 per cent) sulphuric acid in a graduated narrow-neck stoppered Babcock flask, and place in ice water and cool. Add slowly 5 c.c. of the turpentine to be tested. Gradually mix the contents, cooling from time to time and not allowing the temperature to rise above 60° C. When the mixture no longer warms up on mixing, agitate and heat on a water bath at from 60° to 65° C. for ten minutes, keeping the contents well mixed by shaking five or six times during the heating. Do not stopper after the turpentine has been added, as it may explode. Cool to room temperature and add concentrated sulphuric acid till the unpolymerized portion rises into the graduated neck. Centrifuge at about 1200 revolutions per minute from four to five minutes, or allow the flask and contents to stand 12 hours. Read the unpolymerized portion, notice its consistency and color and determine its refractive index.

**39. Pine oil and heavy turpentine.** The large increase in the use of petroleum thinners, in the paint and varnish industry, has resulted in a corresponding decrease in the demand for turpentine and has like-



wise restricted the consumption of the heavy refined distillates, known to the trade as pine oil. On account of this limited demand these products have not become definitely standardized, and unless the constants, especially the specific gravity and the distillation figures, are specified, the purchaser may receive, under the name of pine oil, distillates varying in gravity from 0.880 to 0.940 with corresponding variations in distillation figures and working properties of the paint, enamel, or varnish in which the pine oil is used. Table IV gives the distillation figures of four different samples of pine oil submitted to the author for examination within one month. This table clearly indicates the lack of standardization referred to above. The advantages to be derived from the use of pine oil are discussed at length by Toch.<sup>1</sup>

**40. Requirements.** A pine oil, to be acceptable, should have a pleasant, aromatic odor, suggestive of camphor or juniper seed, and a coefficient of evaporation suited to the requirements of the paint, enamel or varnish in question. An insufficiently refined oil will cause serious complaint, when used in finishes for interior work, on account of the obnoxious odor, during the drying, due to the empyreumatic compounds present.

**41. Presence of water.** The pine oils examined by the author have been found to contain 2-5 per cent of water, which for certain purposes is beneficial and, except when used in nitro-cellulose lacquers, has not been found to be detrimental. The degree of cloudiness manifested when two parts of pine oil are mixed with one part of naphtha is indicative of the amount of water present.

<sup>1</sup> Jour. Ind. Eng. Chem., Vol. VI, page 720.



TABLE IV

## 42. Distillation of pine oils by the author

Temperature	I Per cent	II Per cent	III Per cent
100° to 150° C.....	2.0	.....	2.0
150 " 170.....	3.0	.....	.....
170 " 180.....	22.0	.....	.....
180 " 190.....	26.0	.....	.....
190 " 200.....	20.0	5.0	7.0
200 " 210.....	18.0	14.0	1.5
210 " 220.....	8.0	51.5	1.5
220 " 230.....	1.0	15.5	1.5
230 " 240.....	.....	5.5	2.0
240 " 250.....	.....	4.0	2.0
250 " 260.....	.....	2.0	2.0
Residue.....	.....	2.5	80.5
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

**43. Examination in paint products.** Owing to the high boiling fractions present in pine oil, it can be removed for estimation from a paint or enamel only with much difficulty, requiring at least two hours treatment with steam as described in Chapter XIII. The specific gravity of the distillate should be noted and the rate of evaporation determined by superimposing 3 drops of the oil on a sheet of dry paper. Polymerization with sulphuric acid does not yield satisfactory results.

TABLE V

44. Analysis of pine oils <sup>1</sup>

Color	I Faintly Yellow	II Nearly Water White	III Water White	IV Straw Color	V Amber Pale
Sp. Gr. 15.5° C....	0.9423	0.9427	0.9338	0.9330	0.9291
Acid value.....	0.68	0.29	0.51	0.59	0.49
Iodine value.....	142.5	118.4	125.4	161.5	173.9
Flash point ° F....	170°	175°	145°	160°	148°
Per cent loss on steam bath after 9 hrs.....	93.4	96.3	97.3	93.8	85.7

<sup>1</sup> J. Md. & Chem. Eng. Chem., Vol. VI, No. 9, page 722.

TABLE V

## 45. Analysis of pine oils (Continued)

Color	VI Straw Color	VII Water White	VIII Straw Color	IX Water White
Sp. gr. 15.5° C.....	0.9355	0.9382	0.9350	0.9383
Acid value.....	0.70	0.17	0.73	0.27
Iodine value.....	143.2	129.8	142.7	124.4
Flash point ° F.....	168°	175°	160°	176°
Per cent loss on steam bath after 9 hrs.....	92.7	98.6	95.1	98.7

TABLE VI

46. Fractional distillation of commercial pine oil <sup>1</sup>

Temperature	Fraction in per cent	Total Distil- late per cent	Sp. Gr. 15.5° C. of fractions
Water 100°.....	2	2	....
174°-194°.....	5	7	0.882
194°-205°.....	11	18	0.920
205°-208°.....	10	28	0.933
208°-210°.....	25	53	0.939
210°-213°.....	35	88	0.941
213°-216°.....	6	94	0.942
216°-218°.....	1	95	0.942
218°-000.....	4	99	....

<sup>1</sup> *Ibid.*, page 723.

## CHAPTER IV

### ALCOHOLS AND ACETONES

**47. Wood alcohol, characteristics.** Wood alcohol, to be acceptable for the manufacture of paint and varnish removers, shellac, stains, etc., should contain at least 97 per cent alcohol and should not have a raw pungent odor. For use in the manufacture of nitro-cellulose lacquers, 99 per cent alcohol should be used.

**48. Impurities.** Acetone, the heavy ketones and methyl acetate may be present in an insufficiently refined alcohol. These impurities may be estimated as described in this chapter.

**49. Specific gravity.** Where only a close approximation of results is required, the gravity or proof can be obtained by following the procedure and tables for denatured alcohol. Accurate results may be obtained by determining the specific gravity with a picnometer at 15.5° C. and using the following table, No. VII.

**50. The uses of denatured alcohol.** Denatured alcohol is used in the manufacture of shellac and other spirit varnishes, in stains, graining compounds, and occasionally in emulsions for mixed paints to prevent freezing.

**51. Composition.** Unless otherwise provided for, alcohol is completely denatured under either of the following formulas:

1. To every 100 parts by volume of ethyl alcohol of the desired proof (not less than 180°) there shall be added 100 parts by volume of approved benzine.

TABLE VII

52. Specific gravity at  $\frac{15^\circ}{15^\circ}$  C. of mixtures (by volume) of methyl alcohol and water<sup>1</sup>

Per Cent Methyl Alcohol by Volume at 15° C.	D $\frac{15^\circ}{15^\circ}$ C.	Per Cent Methyl Alcohol by Volume at 15° C.	D $\frac{15^\circ}{15^\circ}$ C.	Per Cent by Weight	Per Cent by Volume at 15° C.	Per Cent by Weight	Per Cent by Volume at 15° C.
0	1.00000	50	0.93326	0	0.000	50	57.712
1	.99851	51	.93155	1	1.253	51	58.739
2	.99703	52	.92982	2	2.502	52	59.759
3	.99560	53	.92806	3	3.746	53	60.773
4	.99422	54	.92626	4	4.986	54	61.781
5	.99283	55	.92443	5	6.222	55	62.783
6	.99146	56	.92256	6	7.454	56	63.778
7	.99011	57	.92067	7	8.682	57	64.767
8	.98877	58	.91877	8	9.907	58	65.750
9	.98746	59	.91682	9	11.128	59	66.725
10	.98621	60	.91483	10	12.345	60	67.693
11	.98496	61	.91282	11	13.559	61	68.654
12	.98370	62	.91079	12	14.770	62	69.607
13	.98247	63	.90873	13	15.977	63	70.552
14	.98125	64	.90663	14	17.181	63	71.490
15	.98003	65	.90450	15	18.382	65	72.420
16	.97884	66	.90234	16	19.579	66	73.344
17	.97766	67	.90014	17	20.773	67	74.262
18	.97648	68	.89790	18	21.963	68	75.172
19	.97530	69	.89561	19	23.149	69	76.077
20	.97413	70	.89327	20	24.332	70	76.976
21	.97295	71	.89088	21	25.512	71	77.864
22	.97177	72	.88844	22	26.688	72	78.746
23	.97058	73	.88596	23	27.860	73	79.618
24	.96936	74	.88346	24	29.029	74	80.480
25	.96820	75	.88092	25	30.193	75	81.336
26	.96700	76	.87836	26	31.354	76	82.182
27	.96580	77	.87578	27	32.510	77	83.022
28	.96459	78	.87312	28	33.662	78	83.855
29	.96338	79	.87040	29	34.809	79	84.680
30	.96216	80	.86760	30	35.952	80	85.499
31	.96091	81	.86474	31	37.091	81	86.310
32	.95966	82	.86180	32	38.224	82	87.110
33	.95838	83	.85883	33	39.352	83	87.899
34	.95708	84	.85582	34	40.476	84	88.677

<sup>1</sup> Circular No. 19 of the Bureau of Standards, pages 23-24.

TABLE VII (Continued)

Per Cent Methyl Alcohol by Volume at 15° C.	D $\frac{15^\circ}{15^\circ}$ C.	Per Cent Methyl Alcohol by Volume at 15° C.	D $\frac{15^\circ}{15^\circ}$ C.	Per Cent by Weight	Per Cent by Volume at 15° C.	Per Cent by Weight	Per Cent by Volume at 15° C.
35	.95576	85	.85276	35	41.594	85	89.448
36	.95443	86	.84967	36	42.708	86	90.212
37	.95308	87	.84646	37	43.816	87	90.968
38	.95170	88	.84314	38	44.919	88	91.716
39	.95029	89	.83971	39	46.016	89	92.456
40	.94886	90	.83623	40	47.109	90	93.188
41	.94741	91	.83269	41	48.195	91	93.912
42	.94593	92	.82907	42	49.277	92	94.627
43	.94443	93	.82538	43	50.353	93	95.326
44	.94291	94	.82163	44	51.422	94	96.017
45	.94136	95	.81772	45	52.486	95	96.697
46	.93979	96	.81363	46	53.544	96	97.370
47	.93820	97	.80942	47	54.595	97	98.039
48	.93657	98	.80514	48	55.639	98	98.696
49	.93493	99	.80082	49	56.678	99	99.351
50	.93326	100	.79647	50	57.712	100	100.000

2. To every 100 parts by volume of ethyl alcohol of the desired proof (not less than 180°) there shall be added 2 parts by volume of approved wood alcohol and one-half part by volume of approved pyridin bases.

The Commissioner of Internal Revenue has authorized the use of one *specialty denatured alcohol* for the manufacture of shellac varnishes, wood finishes and varnish removers. The denaturing in this case is accomplished by adding 5 gallons of approved wood alcohol to 100 gallons ethyl alcohol.

**53. Proof spirit.**<sup>1</sup> Proof spirit is held and taken to be that alcoholic liquor which contains one-half its volume of alcohol of a specific gravity of seven thou-

<sup>1</sup> Gaugers' Manual, U. S. Internal Revenue, page 413.

sand nine hundred and thirty-nine ten-thousandths (0.7939), at 60° Fahrenheit, referred to water at 60° Fahrenheit as unity. Proof spirit has at 60° Fahrenheit a specific gravity of 0.93426, 100 parts by volume of the same consisting of 50 parts of absolute alcohol and 53.71 parts of water. The difference of the sum of the parts of alcohol and water and the resulting 100 parts of proof spirit is due to the contraction which takes place when alcohol and water combine.

**54. Correction for temperature.** It is seldom, however, that the alcohol is inspected at 60° F.; and as its density varies with the temperature, a correction is necessary for a temperature differing from 60°, the hydrometer giving too low an indication for temperatures below 60° and too high for those above. This correction, applied to the indication of the hydrometer, gives the true per cent, or what the reading of the hydrometer would be were the alcohol at 60°.

**55. Hydrometer to be used.** In 1913 a new style of hydrometer was prescribed for use by the Internal Revenue Department. For ordinary use a No. 7 stem (157° to 181° proof) and a No. 8 stem (177° to 200° proof) are sufficient.

**56. Determination.** The sample is poured into a cylinder, sufficient space being left for the displacement of the liquid when the stem is inserted, and the hydrometer carefully placed therein. The eye should be held slightly below the level of the liquid, and the highest immersed reading on the stem is taken as the apparent indication. The thermometer should be placed in the liquid and read immediately after the reading of the proof indication. The true proof will be determined by reference to the following table.



The left-hand column, headed "Indication," contains the reading of the hydrometer, and on the same horizontal line, in the body of the table, in the "Temperature" column indicated by the thermometer, is found the corrected reading or true per cent of proof which, divided by 2, gives the percentage of alcohol present.

TABLE VIII

## 57. True per cent of proof for temperatures between 51° F. and 60° F.

Indication.	51° F.	52° F.	53° F.	54° F.	55° F.	56° F.	57° F.	58° F.	59° F.	60° F.
161	163.9	163.6	163.2	162.9	162.6	162.3	162.0	161.6	161.3	161.0
162	164.9	164.6	164.2	163.9	163.6	163.3	163.0	162.6	162.3	162.0
163	165.9	165.6	165.2	164.9	164.6	164.3	164.0	163.6	163.3	163.0
164	166.9	166.6	166.2	165.9	165.6	165.3	165.0	164.6	164.3	164.0
165	167.9	167.6	167.2	166.9	166.6	166.3	166.0	165.6	165.3	165.0
166	168.9	168.6	168.2	167.9	167.6	167.3	167.0	166.6	166.3	166.0
167	169.8	169.5	169.2	168.9	168.6	168.3	168.0	167.6	167.3	167.0
168	170.8	170.5	170.2	169.9	169.6	169.3	169.0	168.6	168.3	168.0
169	171.8	171.5	171.2	170.9	170.6	170.3	170.0	169.6	169.3	169.0
170	172.8	172.5	172.2	171.9	171.6	171.3	171.0	170.6	170.3	170.0
171	173.8	173.5	173.2	172.9	172.6	172.3	172.0	171.6	171.3	171.0
172	174.7	174.4	174.1	173.8	173.5	173.2	172.9	172.6	172.3	172.0
173	175.6	175.3	175.1	174.8	174.5	174.2	173.9	173.6	173.3	173.0
174	176.6	176.3	176.1	175.8	175.5	175.2	174.9	174.6	174.3	174.0
175	177.6	177.3	177.1	176.8	176.5	176.2	175.9	175.6	175.3	175.0
176	178.6	178.3	178.1	177.8	177.5	177.2	176.9	176.6	176.3	176.0
177	179.6	179.3	179.1	178.8	178.5	178.2	177.9	177.6	177.3	177.0
178	180.5	180.2	180.0	179.7	179.4	179.1	178.8	178.6	178.3	178.0
179	181.4	181.2	180.9	180.7	180.4	180.1	179.8	179.6	179.3	179.0
180	182.4	182.2	181.9	181.7	181.4	181.1	180.8	180.6	180.3	180.0
181	183.4	183.2	182.9	182.7	182.4	182.1	181.8	181.6	181.3	181.0
182	184.4	184.2	183.9	183.7	183.4	183.1	182.8	182.6	182.3	182.0
183	185.4	185.2	184.9	184.7	184.4	184.1	183.8	183.6	183.3	183.0
184	186.3	186.1	185.8	185.6	185.3	185.0	184.8	184.5	184.3	184.0
185	187.3	187.1	186.8	186.6	186.3	186.0	185.8	185.5	185.3	185.0
186	188.3	188.0	187.8	187.5	187.3	187.0	186.8	186.5	186.3	186.0
187	189.2	189.0	188.7	188.5	188.3	188.0	187.8	187.5	187.3	187.0
188	190.2	190.0	189.7	189.5	189.3	189.0	188.8	188.5	188.3	188.0
189	191.1	190.9	190.6	190.4	190.2	190.0	189.7	189.5	189.2	189.0
190	192.1	191.9	191.6	191.4	191.2	191.0	190.7	190.5	190.2	190.0
191	193.1	192.9	192.6	192.4	192.2	192.0	191.7	191.5	191.2	191.0
192	194.0	193.8	193.6	193.4	193.2	193.0	192.7	192.5	192.2	192.0
193	195.0	194.8	194.6	194.4	194.2	194.0	193.7	193.5	193.2	193.0
194	196.0	195.8	195.6	195.4	195.2	195.0	194.7	194.5	194.2	194.0
195	196.9	196.7	196.5	196.3	196.1	195.9	195.7	195.4	195.2	195.0
196	197.9	197.7	197.5	197.3	197.1	196.9	196.7	196.4	196.2	196.0
197	198.8	198.7	198.5	198.3	198.1	197.9	197.7	197.4	197.2	197.0
198	199.9	199.7	199.5	199.3	199.1	198.9	198.7	198.4	198.2	198.0
199	.....	.....	.....	.....	200.0	199.8	199.6	199.4	199.2	199.0
						.....	.....	.....	.....	200.0

True per cent of proof for temperatures between 61° F. and 70° F.

Indica- tion.	61° F.	62° F.	63° F.	64° F.	65° F.	66° F.	67° F.	68° F.	69° F.	70° F.
161	160.7	160.3	160.0	159.6	159.3	159.0	158.7	158.3	158.0	157.7
162	161.7	161.3	161.0	160.6	160.3	160.0	159.7	159.3	159.0	158.7
163	162.7	162.4	162.0	161.7	161.4	161.1	160.7	160.4	160.0	159.7
164	163.7	163.4	163.0	162.7	162.4	162.1	161.7	161.4	161.0	160.7
165	164.7	164.4	164.0	163.7	163.4	163.1	162.7	162.4	162.0	161.7
166	165.7	165.4	165.0	164.7	164.4	164.1	163.7	163.4	163.0	162.7
167	166.7	166.4	166.0	165.7	165.4	165.1	164.8	164.4	164.1	163.8
168	167.7	167.4	167.0	166.7	166.4	166.1	165.8	165.4	165.1	164.8
169	168.7	168.4	168.0	167.7	167.4	167.1	166.8	166.4	166.1	165.8
170	169.7	169.4	169.0	168.7	168.4	168.1	167.8	167.4	167.1	166.8
171	170.7	170.4	170.0	169.7	169.4	169.1	168.8	168.4	168.1	167.8
172	171.7	171.4	171.0	170.7	170.4	170.1	169.8	169.5	169.2	168.9
173	172.7	172.4	172.1	171.8	171.5	171.2	170.9	170.5	170.2	169.9
174	173.7	173.4	173.1	172.8	172.5	172.2	171.9	171.5	171.2	170.9
175	174.7	174.4	174.1	173.8	173.5	173.2	172.9	172.6	172.3	172.0
176	175.7	175.4	175.1	174.8	174.5	174.2	173.9	173.6	173.3	173.0
177	176.7	176.4	176.1	175.8	175.5	175.2	174.9	174.7	174.4	174.1
178	177.7	177.4	177.1	176.8	176.5	176.2	175.9	175.7	175.4	175.1
179	178.7	178.4	178.1	177.8	177.5	177.2	176.9	176.7	176.4	176.1
180	179.7	179.4	179.2	178.9	178.6	178.3	178.0	177.7	177.4	177.1
181	180.7	180.4	180.2	179.9	179.6	179.3	179.0	178.8	178.5	178.2
182	181.7	181.4	181.2	180.9	180.6	180.3	180.0	179.8	179.5	179.2
183	182.7	182.4	182.2	181.9	181.6	181.3	181.0	180.8	180.5	180.2
184	183.7	183.4	183.2	182.9	182.6	182.3	182.0	181.8	181.5	181.2
185	184.7	184.4	184.2	183.9	183.6	183.3	183.1	182.8	182.6	182.3
186	185.7	185.5	185.2	185.0	184.7	184.4	184.1	183.9	183.6	183.3
187	186.7	186.5	186.2	186.0	185.7	185.4	185.1	184.9	184.6	184.3
188	187.8	187.5	187.3	187.0	186.8	186.5	186.2	186.0	185.7	185.4
189	188.8	188.5	188.3	188.0	187.8	187.5	187.3	187.0	186.8	186.5
190	189.8	189.5	189.3	189.0	188.8	188.6	188.3	188.1	187.8	187.6
191	190.8	190.5	190.3	190.0	189.8	189.6	189.3	189.1	188.8	188.6
192	191.8	191.6	191.3	191.1	190.9	190.7	190.4	190.2	189.9	189.7
193	192.8	192.6	192.3	192.1	191.9	191.7	191.4	191.2	190.9	190.7
194	193.8	193.6	193.3	193.1	192.9	192.7	192.4	192.2	191.9	191.7
195	194.8	194.6	194.3	194.1	193.9	193.7	193.5	193.2	193.0	192.8
196	195.8	195.6	195.3	195.1	194.9	194.7	194.5	194.2	194.0	193.8
197	196.8	196.6	196.4	196.2	196.0	195.8	195.5	195.3	195.0	194.8
198	197.8	197.6	197.4	197.2	197.0	196.8	196.6	196.3	196.1	195.9
199	198.8	198.6	198.4	198.2	198.0	197.8	197.6	197.3	197.1	196.9
200	199.8	199.6	199.4	199.2	199.0	198.8	198.6	198.3	198.1	197.9

True per cent of proof for temperatures between 71° F. and 80° F.

Indica- tion.	71° F.	72° F.	73° F.	74° F.	75° F.	76° F.	77° F.	78° F.	79° F.	80° F.
161	157.4	157.0	156.7	156.3	156.0	155.6	155.3	154.9	154.6	154.2
162	158.4	158.0	157.7	157.3	157.0	156.7	156.3	156.0	155.6	155.3
163	159.4	159.0	158.7	158.3	158.0	157.7	157.3	157.0	156.6	156.3
164	160.4	160.0	159.7	159.3	159.0	158.7	158.3	158.0	157.6	157.3
165	161.4	161.1	160.7	160.4	160.1	159.8	159.4	159.1	158.7	158.4
166	162.4	162.1	161.7	161.4	161.1	160.8	160.4	160.1	159.7	159.4
167	163.5	163.1	162.8	162.4	162.1	161.8	161.4	161.1	160.7	160.4
168	164.5	164.1	163.8	163.4	163.1	162.8	162.5	162.1	161.8	161.5
169	165.5	165.2	164.8	164.5	164.2	163.9	163.5	163.2	162.8	162.5
170	166.5	166.2	165.8	165.5	165.2	164.9	164.5	164.2	163.8	163.5
171	167.5	167.2	166.8	166.5	166.2	165.9	165.6	165.2	164.9	164.6
172	168.6	168.2	167.9	167.5	167.2	166.9	166.6	166.2	165.9	165.6
173	169.6	169.3	168.9	168.6	168.3	168.0	167.7	167.3	167.0	166.7
174	170.6	170.3	169.9	169.6	169.3	169.0	168.7	168.3	168.0	167.7
175	171.7	171.4	171.0	170.7	170.4	170.1	169.8	169.4	169.1	168.8
176	172.7	172.4	172.0	171.7	171.4	171.1	170.8	170.4	170.1	169.8
177	173.8	173.5	173.1	172.8	172.5	172.2	171.9	171.5	171.2	170.9
178	174.8	174.5	174.1	173.8	173.5	173.2	172.9	172.6	172.3	172.0
179	175.8	175.5	175.2	174.9	174.6	174.3	174.0	173.6	173.3	173.0
180	176.8	176.5	176.2	175.9	175.6	175.3	175.0	174.7	174.4	174.1
181	177.9	177.6	177.3	177.0	176.7	176.4	176.1	175.8	175.5	175.2
182	178.9	178.6	178.3	178.0	177.7	177.4	177.1	176.8	176.5	176.2
183	179.9	179.6	179.4	179.1	178.8	178.5	178.2	177.9	177.6	177.3
184	180.9	180.6	180.4	180.1	179.8	179.5	179.2	179.0	178.7	178.4
185	182.0	181.7	181.4	181.1	180.8	180.5	180.2	180.0	179.7	179.4
186	183.0	182.7	182.5	182.2	181.9	181.6	181.3	181.1	180.8	180.5
187	184.0	183.8	183.5	183.3	183.0	182.7	182.4	182.1	181.8	181.5
188	185.1	184.9	184.6	184.4	184.1	183.8	183.5	183.2	182.9	182.6
189	186.2	186.0	185.7	185.5	185.2	184.9	184.6	184.4	184.1	183.8
190	187.3	187.1	186.8	186.6	186.3	186.0	185.8	185.5	185.3	185.0
191	188.4	188.1	187.9	187.6	187.4	187.1	186.9	186.6	186.4	186.1
192	189.4	189.2	188.9	188.7	188.4	188.2	187.9	187.7	187.4	187.2
193	190.5	190.2	190.0	189.7	189.5	189.3	189.0	188.8	188.5	188.3
194	191.5	191.3	191.0	190.8	190.6	190.4	190.1	189.9	189.6	189.4
195	192.6	192.3	192.1	191.8	191.6	191.4	191.2	190.9	190.7	190.5
196	193.6	193.4	193.1	192.9	192.7	192.5	192.2	192.0	191.7	191.5
197	194.6	194.4	194.1	193.9	193.7	193.5	193.3	193.0	192.8	192.6
198	195.7	195.5	195.2	195.0	194.8	194.6	194.4	194.1	193.9	193.7
199	196.7	196.5	196.3	196.1	195.9	195.7	195.5	195.2	194.9	194.7
200	197.7	197.5	197.3	197.1	196.9	196.7	196.5	196.2	196.0	195.8

True per cent of proof for temperatures between 81° F. and 90° F.

Indica- tion	81° F.	82° F.	83° F.	84° F.	85° F.	86° F.	87° F.	88° F.	89° F.	90° F.
161	153.9	153.5	153.2	152.8	152.5	152.1	151.7	151.4	151.0	150.6
162	154.9	154.6	154.2	153.9	153.5	153.1	152.8	152.4	152.1	151.7
163	156.0	155.6	155.3	154.9	154.6	154.2	153.9	153.5	153.2	152.8
164	157.0	156.6	156.3	155.9	155.6	155.2	154.9	154.5	154.2	153.8
165	158.0	157.7	157.3	157.0	156.6	156.3	155.9	155.6	155.2	154.9
166	159.1	158.7	158.4	158.0	157.7	157.3	157.0	156.6	156.3	155.9
167	160.1	159.7	159.4	159.0	158.7	158.4	158.0	157.7	157.3	157.0
168	161.1	160.8	160.4	160.1	159.7	159.4	159.0	158.7	158.3	158.0
169	162.2	161.8	161.5	161.1	160.8	160.5	160.1	159.8	159.4	159.1
170	163.2	162.8	162.5	162.1	161.8	161.5	161.1	160.8	160.4	160.1
171	164.3	163.9	163.6	163.2	162.9	162.6	162.2	161.9	161.5	161.2
172	165.3	165.0	164.6	164.3	164.0	163.7	163.3	163.0	162.6	162.3
173	166.4	166.0	165.7	165.3	165.0	164.7	164.3	164.0	163.6	163.3
174	167.4	167.1	166.7	166.4	166.1	165.8	165.4	165.1	164.7	164.4
175	168.5	168.2	167.8	167.5	167.2	166.9	166.5	166.2	165.8	165.5
176	169.5	169.2	168.9	168.6	168.3	168.0	167.6	167.3	166.9	166.6
177	170.6	170.3	169.9	169.6	169.3	169.0	168.7	168.3	168.0	167.7
178	171.7	171.4	171.0	170.7	170.4	170.1	169.8	169.4	169.1	168.8
179	172.7	172.4	172.1	171.8	171.5	171.2	170.9	170.5	170.2	169.9
180	173.8	173.5	173.2	172.9	172.6	172.3	172.0	171.6	171.3	171.0
181	174.9	174.6	174.3	174.0	173.7	173.4	173.1	172.7	172.4	172.1
182	175.9	175.6	175.3	175.0	174.7	174.4	174.1	173.8	173.5	173.2
183	177.0	176.7	176.4	176.1	175.8	175.5	175.2	174.9	174.6	174.3
184	178.1	177.8	177.5	177.2	176.9	176.6	176.3	176.0	175.7	175.4
185	179.1	178.8	178.6	178.3	178.0	177.7	177.4	177.0	176.7	176.4
186	180.2	179.9	179.6	179.3	179.0	178.7	178.4	178.1	177.8	177.5
187	181.2	180.9	180.7	180.4	180.1	179.8	179.5	179.2	178.9	178.6
188	182.3	182.0	181.8	181.5	181.2	180.9	180.6	180.4	180.1	179.8
189	183.5	183.2	183.0	182.7	182.4	182.1	181.8	181.5	181.2	180.9
190	184.7	184.4	184.1	183.8	183.5	183.2	182.9	182.7	182.4	182.1
191	185.8	185.5	185.2	184.9	184.6	184.3	184.0	183.8	183.5	183.2
192	186.9	186.6	186.4	186.1	185.8	185.5	185.2	185.0	184.7	184.4
193	188.0	187.8	187.5	187.3	187.0	186.7	186.4	186.2	185.9	185.6
194	189.1	188.9	188.6	188.4	188.1	187.8	187.6	187.3	187.1	186.8
195	190.2	190.0	189.7	189.5	189.2	188.9	188.7	188.4	188.2	187.9
196	191.3	191.0	190.8	190.5	190.3	190.0	189.8	189.5	189.3	189.0
197	192.4	192.1	191.9	191.6	191.4	191.2	190.9	190.7	190.4	190.2
198	193.5	193.2	193.0	192.7	192.5	192.3	192.0	191.8	191.5	191.3
199	194.5	194.3	194.0	193.8	193.6	193.4	193.1	192.9	192.6	192.4
200	195.6	195.4	195.1	194.9	194.7	194.5	194.2	194.0	193.7	193.5

58. Estimation of methyl alcohol in mixtures with ethyl alcohol. The method of Thorp & Holmes given below has proven very satisfactory. If a Zeiss immersion refractometer be accessible, the method of Leach and Lythgoe<sup>1</sup> is to be preferred, as it is more rapid and convenient, and equally satisfactory. If the

<sup>1</sup> J. Am. Chem. Soc., 1905, 27, 964.



alcoholic mixture to be examined contains acetone, acetone oils or other solvents, it is advisable to follow the method of Knight and Lincoln, *S. Ind. and Eng. Chem.* 7, page 837.

The Thorp and Holmes method depends upon the fact that in the presence of potassium dichromate and sulphuric acid, in a closed vessel at  $100^{\circ}$ , ethyl alcohol is converted into its theoretical equivalent of acetic acid, while with methyl alcohol, the product resulting from the oxidation is always carbon dioxide and water. It has, however, been found that for each gram of ethyl alcohol present in the solution, 0.01 gram of carbon dioxide may be formed, and this correction should be made in all determinations.

The specific gravity is determined by means of a pycnometer. The total per cent of the alcohol is practically the same as the per cent of ethyl alcohol of the same specific gravity.

The methyl alcohol is determined by converting it into carbon dioxide by means of sulphuric acid and potassium dichromate in the Knorrs' apparatus.

**59. Procedure.** Weigh into the flask 20 grams of potassium dichromate, connect the apparatus after having weighed the soda-lime tubes. Introduce through the stop-cock funnel an exact volume of the alcohols not to exceed 4 grams of the mixed alcohols, and an amount of water equal to 50 c.c., less the number of c.c. of alcoholic solution; 80 c.c. of sulphuric acid (made by diluting one volume of concentrated acid with four volumes of water) are added, well shaken and allowed to stand 18 hours. Dissolve 10 grams of potassium dichromate in 50 c.c. of water, add through the funnel; then add 50 c.c. of concentrated sulphuric acid and heat the contents of the

flask to boiling for about ten minutes, the carbon dioxide being carried off by a current of air through the apparatus. The heat is now removed and the current of air continued for a few minutes longer. Disconnect and weigh the soda-lime tubes.

Calculate the methyl alcohol from the proportion

$$1.373 : 1 :: \text{wt. CO}_2 \text{ obtained} : x$$

$$x = \text{wt. methyl alcohol,}$$

the theoretical oxidation of 1 gram methyl alcohol producing 1.373 grams of carbon dioxide.

#### EXAMPLE

Specific gravity of sample.....	0.7992
Weight of sample used.....	1.0118 grams
Weight of carbon dioxide.....	1.3810 grams
$1.373 : 1 :: 1.3810 : x$	
$x = 1.006 \text{ grams methyl alcohol.}$	
$1.0118 : 1.1006 :: 100 : y$	
$y = 99.4 \text{ per cent methyl alcohol.}$	

**60. Correction.** If ethyl alcohol is present, the correction previously referred to, of 0.01 gram carbon dioxide for each gram of ethyl alcohol, should always be applied. The weight of the methyl alcohol subtracted from the weight of the mixed alcohols (calculated from the sp. gr.) gives weight of the ethyl alcohol, approximately. The weight obtained multiplied by 0.01 gives correction to be deducted from the total carbon dioxide, for the recalculation of the weight of methyl alcohol. It is obvious that a very slight error is thus introduced, but the writer believes that it is so small that it may be safely neglected.

**61. Acetone uses.** Commercially pure acetone is not used to any extent in the paint and varnish industries except in nitro-cellulose lacquers. Admixed with methyl alcohol it is used extensively in the preparation of paint and varnish removers. The usual stan-



dard mixtures of alcohol and acetone used for this purpose are approximately as follows:

1. Acetone 25 per cent, methyl alcohol 75 per cent.  
Sp. Gr. approximately 0.804.
2. Acetone 50 per cent, methyl alcohol 50 per cent.  
Sp. Gr. approximately 0.807.

This grade contains from a trace up to 2 per cent of methyl acetate.

3. Acetone 50 per cent, methyl acetate 15 per cent  
and methyl alcohol 35 per cent.

The above grades frequently vary in composition. The first grade may contain methyl acetate up to 6 per cent, and the acetone content may vary from 24 to 29 per cent. The first two grades may have specific gravities as high as 0.823, due to the presence of aldehyde bodies of unknown composition which possess a pungent disagreeable odor and vigorously attack the workers' hands when used in paint and varnish removers. The specific gravity of pure methyl alcohol is 0.796, of pure acetone 0.797, and of methyl acetate 0.964 at 15.5° C.

**62. Acetone content, Messinger's method.** One c.c. of a mixture of 10 c.c. of acetone and 90 c.c. of water is treated with 10 c.c. of twice normal soda solution and allowed to stand 5 minutes. Then an accurately measured portion of 50–100 c.c., depending on the amount of acetone present, of N/10 iodine solution is added while shaking. The solution is made just acid with dilute sulphuric acid ten minutes after the addition of the iodine solution. The excess iodine is titrated at once with tenth-normal sodium thio-sulphate, using a few drops of starch solution as

an indicator. The solution should be kept at a temperature of from 15°–20° C.

Calculation:

$X$  = grams of acetone in 100 c.c. spirit.

$Y$  = number c.c. of N/10 iodine required.

$N$  = volume of sample taken for titration.

$$\text{Then } X = n \frac{Y \times 0.096672}{N}.$$

The author has found that this method gives very satisfactory results. It is essential, however, that the temperature be kept closely at 15° C. and the time limit, of ten minutes, between the addition of the iodine solution and the titration with the thiosulphate, be adhered to, otherwise varying results will be obtained. Usually it will be found more convenient to take 5 c.c. of the acetone to be tested, diluting to 500 c.c. and taking a sample of this mixture for the determination.

**63. Methyl acetate.**<sup>1</sup> Five c.c. of the sample are run into a flask, and ten c.c. normal sodium hydroxide free from carbonate are added. The flask connected to a return condenser is heated and the contents kept boiling for two hours. Instead of digesting at the boiling temperature, the flask may be allowed to stand overnight at room temperature and then heated on the steam bath for thirty minutes connected with an ordinary tube condenser. The liquid after digestion is cooled and titrated with normal sulphuric acid, using phenolphthalein as an indicator.

$$\begin{aligned} \text{Methyl acetate} &= \text{grams per 100 c.c. of sample} \\ &= \frac{.074 \times \text{c.c. of N/1 soda soln. required} \times 100}{\text{c.c. of sample taken.}} \end{aligned}$$

<sup>1</sup> Regulations No. 30 revised, U. S. Internal Revenue, page 46.

The author has found that instead of boiling with a return condenser, the use of a pressure flask heated for thirty minutes in boiling water gives more uniform results.

**64. Acetone oils.** In the manufacture of wood alcohol and acetone, a number of higher ketones are obtained. These are purified by distillation and put on the market as mixtures having definite distilling ranges. They are used chiefly in the manufacture of special varnishes and lacquers. They have a strong, pungent, characteristic odor, disagreeable to most people. Their solvent value is very high, having a much slower rate of evaporation and, consequently, a longer flow than other lacquer solvents, except fusel oil. They have found a wide use in brushing and dipping lacquers where large surfaces are to be finished. Usually amyl acetate, which is almost always present in these lacquers, masks the odor of the heavy acetone distillates to a considerable degree.

In addition to acetone and hydrocarbons, the following substances have been identified in acetone oils: Methyl ethyl ketone (b. pt.  $79.6^{\circ}\text{C.}$ ), methyl propyl ketone ( $101.7^{\circ}$ ), methyl isopropyl ketone ( $94^{\circ}$ ), methyl n-butyl ketone ( $127.4^{\circ}$ ), cyclopentanone ( $130^{\circ}$ ), and acetaldehyde ( $20.8^{\circ}$ ). All these substances, with the exception of the hydrocarbons, are soluble in sodium bisulphate solutions.

TABLE IX

## 65. Distillation of acetone oils by the author

Temperature	I	II	III
60-70° C.....	6.5	6.0	....
70-80.....	35.0	25.0	....
80-90.....	53.0	28.0	....
90-100.....	5.0	18.5	....
100-110.....	....	8.5	....
110-120.....	....	4.5	....
120-130.....	....	6.0	2.5
130-140.....	....	3.0	4.5
140-150.....	....	0.5	99.5
150-160.....	....	....	16.5
160-170.....	....	....	17.5
170-180.....	....	....	17.0
180-190.....	....	....	9.0
190-200.....	....	....	8.5
200-210.....	....	....	5.0
210-220.....	....	....	4.0
Residue.....	....	....	6.0

## CHAPTER V

### BENZOL AND SOLVENT NAPHTHAS

**66. Uses.** In the paint and varnish industries, benzol finds its chief use in paint and varnish removers on account of its high solvent properties, and in stains to secure proper penetration. The solvent naphthas are used in enamel liquids and baking Japans to prevent "flooding" and to secure the desired "flow" as well as for their great solvent strength. These benzol products should be water-white and free from a disagreeable odor either in the sample or after evaporation from a sheet of filter paper.

**67. Specific gravity.** The specific gravities of the more commonly used benzol products are as follows:

Commercially pure benzol.....	0.875 to 0.885	T-6
100% benzol.....	.875 to .885	
90% benzol.....	.870 to .882	
Solvent naphtha.....	.862 to .872	
Hi-flash naphtha.....	.870 to .880	

The specific gravity may be determined at room temperature and calculated to 15.5° C. by using the coefficient of expansion for benzol, which is 0.00066 per degree Centigrade.

**68. Distillation.** The designation "90% benzol" means that 90 per cent of the entire product will distill under 100° C. It is this grade which is most widely used in the paint industry. The following method of distillation is the one used by one of the large producers of benzol products and has been found very satisfactory by the author.



**69. Procedure.** The flask used for this distillation has a capacity of 200 c.c., the side tube being at the center of the neck. One hundred c.c. of the material is placed in the distilling flask and a thermometer inserted so that the top of its bulb is on a level with the bottom of the side tube. The flask should be placed on an asbestos mat, through which a hole has been cut one inch in diameter, and heat applied direct from a Bunsen burner. The asbestos mat prevents superheating to a great extent. The operator should be careful to remove the source of heat as soon as the last drop of liquid has vaporized. The distillation should be started slowly, finished slowly, and carried on at a rate which should be judged by the manner in which the drops of condensed vapors are coming from the delivery end of the condenser tube. During the major part of the distillation, it should be run at a rate which will just allow individual and separate drops to be formed. A steady stream should at no time flow from the end of the condenser tube. The starting point should be noted and volume readings taken every even  $10^{\circ}$  until the liquid is all distilled.

**70. Solvent naphtha and the higher flash-point naphthas.** These solvents are mixtures of toluol, xyols, and the higher boiling point homologues of benzol. They act as very powerful solvents, especially toward the more difficultly soluble blacks used in high grade baking Japans. Occasionally, crude coal tar naphthas are used in the cheaper baking Japans. Such naphthas distill essentially above  $200^{\circ}\text{C}$ . and usually contain a considerable percentage of naphthalene which crystallizes out in cold weather. These crudes are sold at a low price and frequently contain water which must be removed by settling before they can be added to the

hot Japan. Particular pains are therefore necessary in sampling shipments of these crudes in order to obtain a uniform sample if water be present.

TABLE X

## 71. Distillation of refined solvent naphthas

	Solvent I	Naphtha II	Hi-flash I	Naphtha II
130° C.-140° C.....	2.1	9.3	....	....
140° -150°.....	72.4	54.1	1.5	19.5
150° -160°.....	12.1	24.5	16.5	26.5
160° -170°.....	5.8	8.5	29.2	21.8
170° -180°.....	4.5	3.6	18.8	13.5
180° -190°.....	2.0	....	17.5	13.4
190° -200°.....	1.1	....	14.5	3.5
200° -210°.....	....	....	2.0	1.8
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

72. Evaporation. The comparative evaporation rates of various benzol products are shown in the following table, XI, 2 c.c. of each material having been allowed to evaporate from a metal surface  $3\frac{1}{2}$  inches square under similar conditions.

TABLE XI

Pure benzol.....	10	minutes
100% benzol.....	13 $\frac{1}{2}$	"
90% benzol.....	14	"
Solvent naphtha.....	107	"
Hi-flash naphtha.....	205	"
Turpentine.....	142	"
62° naphtha.....	18	"

## CHAPTER VI

### LINSEED OIL

**73. Uses.** Linseed oil, either raw or treated, constitutes the major portion of the vehicle of nearly all paints and is a most important constituent of the vehicle in most enamels and varnishes. Unfortunately, the specifications under which raw linseed oil is purchased, including those so far adopted by the American Society for Testing Materials, govern the purity of the oil rather than the quality. Linseed oil obtained direct from the crusher will, invariably, be found on examination to be pure, but the quality may be unsatisfactory to the paint manufacturer. This may be due to the presence of excessive amounts of "foots" or to the character of the seed from which the oil is obtained, or both. The determination of the oxygen absorption as described in section 197 frequently gives valuable information regarding the drying value of an oil of questionable purity or suitability.

**74. Raw linseed oil.** The American Society for Testing Materials has adopted standard specifications for the purity of raw linseed oil from North American seed which are as follows:

	Maximum	Minimum
Specific gravity at $\frac{15.5^{\circ}}{15.5^{\circ}}$ C.....	0.936	0.932
or		
Specific gravity at $\frac{25.0^{\circ}}{25.0^{\circ}}$ C.....	0.931	0.927
Acid number.....	6.00	....
Saponification number.....	195.00	189.00
Unsaponifiable matter, per cent.....	1.50	....
Refractive index at $25^{\circ}$ .....	1.4805	1.479
Iodine number (Hanus).....	....	180.00

Commercial shipments of raw linseed oil from a good grade of North American seed will, as a rule, meet these specifications, whereas oil from South American and other foreign-grown flaxseed very often will not, as indicated by the following table, No. XII.

TABLE XII

## 75. Constants for raw linseed oil

	Specific Gravity 15.5° 15.5° C.	Acid No.	Iodine Number Hanus	Saponi- fication	Refrac- tive Index 25° C.
Linseed oil from high grade North Dakota seed, 48 samples <sup>1</sup>					
Average.....	.9331	0.95	185.9	191.3	1.4796
Maximum.....	.9345	3.10	193.1	192.9	1.4805
Minimum.....	.9310	0.38	171.6	189.9	1.4788
Linseed oil from immature North Dakota seed, 4 samples <sup>1</sup>					
Average.....	.9325	1.78	183.2	192.3	1.4795
Maximum.....	.9336	2.80	185.9	192.6	1.4801
Minimum.....	.9310	0.54	175.9	191.9	1.4787
Linseed oil from damp and moldy North Dakota seed, 10 samples <sup>1</sup>					
Average.....	.9331	1.89	183.1	191.9	1.4795
Maximum.....	.9345	2.97	186.4	193.0	1.4802
Minimum.....	.9315	1.22	175.8	190.0	1.4785
Linseed oil from South American seed <sup>2</sup>					
1.....	.9326	1.47	170.8	191.4	1.4785
2.....	.9315	3.54	172.3	190.5	1.4784
3.....	.9329	5.48	179.2	192.4	1.4796
4.....	.9333	6.34	179.0	191.4	1.4795
5.....	.9334	3.91	180.3	190.5	1.4796
Linseed oil from Bombay seed <sup>2</sup> .....	.9336	1.22	179.5	192.6	1.4794
Linseed oil from Calcutta seed <sup>2</sup>					
1.....	.9334	1.26	178.5	191.9	1.4792
2.....	.9334	2.02	176.7	192.1	1.4790
3.....	.9330	1.63	177.8	191.9	1.4791

<sup>1</sup> Washburn, Bulletin 118 N. D. Exp. Station, 1916.<sup>2</sup> Proceedings Am. Soc. for Testing Materials, Vol. XIII, page 376.

**76. South American seed.** Much of the trouble experienced by eastern paint manufacturers during recent years has been laid to the use of oil from South American seed. Samples examined by the author have contained excessive amounts of foots and in practice have been slow in drying with the normal amount of drier used in high grade paints.

**77. Methods of testing prescribed by the American Society for Testing Materials. General.** All tests shall be made on oil which has been filtered at a temperature of between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis.

0-5  
**78. Specific gravity.** Use a pycnometer, accurately standardized and having a capacity of at least 25 c.c., or any other equally accurate method, making a test at 15.5° C., water being 1 at 15.5° C., or a test at 25° C., water being 1 at 25° C.

The author has found it more satisfactory to use a Tagliabue hydrometer reading from .900 to .960, obtaining the gravity at room temperature and calculating to 15° C. with the aid of the following table, No. XIII.<sup>1</sup>

<sup>1</sup> Technologic Paper No. 9, Bureau of Standards, page 20.



TABLE No. XIII

## 79. Density of linseed oil

Tem- pera- ture	Density						
° C							
10	0.9329	0.9339	0.9349	0.9359	0.9369	0.9379	0.9389
11	.9322	.9332	.9342	.9352	.9362	.9372	.9382
12	.9315	.9325	.9335	.9345	.9355	.9365	.9375
13	.9308	.9318	.9328	.9338	.9348	.9358	.9368
14	.9301	.9311	.9321	.9331	.9341	.9351	.9361
15	.9294	.9304	.9314	.9324	.9334	.9344	.9354
16	.9288	.9298	.9308	.9318	.9328	.9338	.9348
17	.9281	.9291	.9301	.9311	.9321	.9331	.9341
18	.9274	.9284	.9294	.9304	.9314	.9324	.9334
19	.9267	.9277	.9287	.9297	.9307	.9317	.9327
20	.9260	.9270	.9280	.9290	.9300	.9310	.9320
21	.9253	.9263	.9273	.9283	.9293	.9303	.9313
22	.9246	.9256	.9266	.9276	.9286	.9296	.9306
23	.9239	.9249	.9259	.9269	.9279	.9289	.9299
24	.9233	.9243	.9253	.9263	.9273	.9283	.9293
25	.9226	.9236	.9246	.9256	.9266	.9276	.9286
26	.9219	.9229	.9239	.9249	.9259	.9269	.9279
27	.9212	.9222	.9232	.9242	.9252	.9262	.9272
28	.9205	.9215	.9225	.9235	.9245	.9255	.9265
29	.9198	.9208	.9218	.9228	.9239	.9248	.9258
30	.9192	.9202	.9212	.9222	.9232	.9242	.9252
31	.9185	.9195	.9205	.9215	.9225	.9235	.9245
32	.9178	.9188	.9198	.9208	.9218	.9228	.9238
33	.9171	.9181	.9191	.9201	.9211	.9221	.9231
34	.9164	.9174	.9184	.9194	.9204	.9214	.9224
35	.9157	.9167	.9177	.9187	.9197	.9207	.9217
36	.9150	.9160	.9170	.9180	.9190	.9200	.9210
37	.9144	.9154	.9164	.9174	.9184	.9194	.9204
38	.9137	.9147	.9157	.9167	.9177	.9187	.9197
39	.9130	.9140	.9150	.9160	.9170	.9180	.9190
40	.9123	.9133	.9143	.9153	.9163	.9173	.9183

0-13

**80. Acid number.** Expressed in milligrams of KOH per gram of oil. Weigh 20 grams of fat or oil into a flask, add 50 c.c. of 95 per cent alcohol which has been neutralized with weak caustic soda, using phenolphthalein as indicator, and heat to the boiling point. Agitate the flask thoroughly, in order to dissolve the free fatty acid as completely as possible. Titrate with tenth-normal alkali, agitating thoroughly, until the pink color persists after vigorous shaking.

Express results either as percentage of oleic acid, as acid degree (cubic centimeters of normal alkali required to neutralize the free acids in 100 grams of oil or fat), or as acid value (milligrams of potassium hydroxide required to saturate the free acids in 1 gram of fat or oil).

(One c.c. of tenth-normal alkali = 0.0282 gram of oleic acid.)

0-14

**81. Saponification number.** Expressed as with acid number. Blanks should also be run to cover effect of alkali in glass.

(a) *Preparation of reagents*

10% NaOH

(1) *Standard sodium hydroxide solution.* Use a tenth-normal solution of sodium hydroxide. Each cubic centimeter contains 0.0040 gram of sodium hydroxide and neutralizes 0.0088 gram of butyric acid.

10% KOH  
75% Ethanol

(2) *Alcoholic potash solution.* Dissolve 40 grams of chemically pure potassium hydroxide in 1 liter of 95 per cent redistilled alcohol.<sup>1</sup> The solution must be clear and the potassium hydroxide free from carbonates.

<sup>1</sup> The alcohol should be redistilled from potassium hydroxide on which it has been standing for some time, or with which it has been boiled for some time, using a reflux condenser.

(3) *Standard acid solution.* Prepare accurately a half-normal solution of hydrochloric acid.

(4) *Indicator.* Dissolve 1 gram of phenolphthalein in 100 c.c. of 95 per cent alcohol.

(b) *Determination*

Conduct the saponification in a wide-mouth Erlenmeyer flask holding from 250 to 300 c.c. Clean thoroughly by washing with water, alcohol, and ether, wipe perfectly dry on the outside and heat for one hour at the temperature of boiling water; allow to cool and weigh.

Run in about 5 grams of the filtered melted fat by means of a pipette, and after cooling again weigh the flask and contents. Pipette 50 c.c. of the alcoholic potash solution into a flask by allowing it to drain for a definite time. Connect the flask with a reflux condenser and boil for 30 minutes or until the fat is completely saponified. Cool and titrate with half-normal hydrochloric acid, using phenolphthalein as indicator. The Koettstorfer number (milligrams of potassium hydroxide required to saponify 1 gram of fat) is obtained as follows: Subtract the number of cubic centimeters of hydrochloric acid used to neutralize the excess of alkali after saponification, from the number of cubic centimeters necessary to neutralize the 50 c.c. of alkali added; multiply the result by 28.06 (the number of milligrams of potassium hydroxide per cubic centimeter) and divide by the number of grams of fat used. Conduct two or three blank experiments, using the same pipette and draining for the same length of time.

**82. Unsaponifiable Matter.** Follow Boemer's method taken from his "Ubbelohde Handbuch der Öle

*7m 100*  
*1 gm phthalein*  
*100 cc 95% alc*

0-30.

u. Fette," pages 261-262. "To 100 g. of oil in a 1000- to 1500-c.c. Erlenmeyer flask add 60 c.c. of an aqueous solution of potassium hydroxide (200 g. KOH dissolved in water and made up to 300 c.c.) and 140 c.c. of 95 per cent alcohol. Connect with a reflux condenser and heat on the water bath, shaking at first until the liquid becomes clear. Then heat for one hour with occasional shaking. Transfer while yet warm to a 2000-c.c. separatory funnel to which some water has been added, wash out the Erlenmeyer with water, using in all 600 c.c. Cool, add 800 c.c. of ether and shake vigorously one minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap and filter the ether (to remove last traces of soap) into a large Erlenmeyer and distill off the ether, adding if necessary one or two pieces of pumice stone. Shake the soap solution three times with 400 c.c. of ether, which add to the first ether extract. To the residue left after distilling the ether add 3 c.c. of the above KOH solution and 7 c.c. of the 95 per cent alcohol, and heat under reflux condenser for 10 minutes on the water bath. Transfer to a small separatory funnel, using 20 to 30 c.c. of water, and after cooling shake out with two portions of 100 c.c. of ether; wash the ether three times with 10 c.c. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distill off the ether, dry residue in water oven and weigh."

0-28 **83. Refractive index.** Use a properly standardized Abbé Refractometer at 25° C., or any other equally accurate instrument.

0-15 **84. Iodine number (Hanus).** (a) *Preparation of reagents.* (1) *Hanus iodine solution.* Dissolve 13.2



grams of iodine in 1000 c.c. of glacial acetic acid (99.5 per cent) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration — 3 c.c. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

(2) *Decinormal sodium thiosulphate solution.* Dissolve 24.8 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter or blotting paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

(3) *Starch paste.* Boil 1 gram of starch in 200 c.c. of distilled water for ten minutes and cool to room temperature.

(4) *Solution of potassium iodide.* Dissolve 150 grams of potassium iodide in water and make up 1 liter.

(5) *Decinormal potassium bichromate.* Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

### (b) Determination

(1) *Standardizing the sodium thiosulphate solution.* Place 20 c.c. of the potassium bichromate solution, to which have been added 10 c.c. of the solution of potassium iodide, in a glass-stoppered flask. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost

6.16 gms K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  
500 H<sub>2</sub>O  
1 1/2 cc. HCl

6.2 gms Na<sub>2</sub>SO<sub>3</sub>  
500 H<sub>2</sub>O

1 gm Starch  
200 cc. H<sub>2</sub>O

15 gms KI  
100 cc H<sub>2</sub>O

2.4541 gms  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  
500 cc H<sub>2</sub>O



disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(2) *Weighing the sample.* Weigh about one-half gram of fat or 0.250 gram of oil<sup>1</sup> on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour onto the crystal, and allow to cool. Introduce the watch crystal into a wide-mouth 16-ounce bottle with ground-glass stopper.

(3) *Absorption of iodine in Hübl's method.* Dissolve the fat or oil in the bottle in 10 c.c. of chloroform. After complete solution has taken place, add 30 c.c. of the iodine solution in the case of fats, or from 40 to 50 c.c.<sup>2</sup> in the case of oils. Place the bottle in a dark place and allow to stand, with occasional shaking, for three hours.<sup>3</sup> This time must be closely adhered to in order to get good results. The excess of iodine should be at least as much as is absorbed.

(4) *Absorption of iodine in Hanus method.* Add 25 c.c. of the iodine solution to the chloroform solution of the fat. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent of the amount added.

(5) *Titration of the unabsorbed iodine.* Add 10 c.c. of the potassium iodide solution in the Hanus method or 20 c.c. in the Hübl method and shake thoroughly;

<sup>1</sup> Use from 0.100 to 0.200 gram in the case of drying oils which have a very high absorbent power.

<sup>2</sup> F. Ulzer (J. Soc. Chem. Ind., 1898, 17:276) says iodine should be in excess, about twice the amount that is absorbed. The solution loses strength with age, but can be used as long as 35 c.c. of tenth-normal thiosulphate neutralize 25 c.c. of iodine solution.

<sup>3</sup> The time allowed does not give the complete iodine absorption power of an oil or fat and cannot be compared with determination in which six to twelve hours have been used. It gives very satisfactory comparative results, but the time factor must be very closely observed.

then add 100 c.c. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(6) *Standardizing the iodine solution by thiosulphate solution.* At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

Per cent of iodine absorbed:

Weight of fat taken.....	gram 0.250
Quantity of iodine solution used.....	c.c. 40.0
Thiosulphate equivalent to iodine used.....	c.c. 65.0
Thiosulphate equivalent to remaining iodine.....	c.c. 40.0
Thiosulphate equivalent to iodine absorbed.....	c.c. 25.0

Per cent of iodine absorbed  $(25.0 \times 0.012692 \times 100)$   
divided by 0.250 = 126.92.

**85. Foots.** The paint specifications adopted by the U. S. Navy, by most of the public service cor-

0-20

porations, and by many of the larger railroad systems, require that the linseed oil used be properly aged, well settled, and free from foots. Gardner (J. Ind. and Eng. Chem., Sept. 1916) vigorously condemns the use of freshly pressed oil containing foots in the manufacture of high grade paints.

Practically all shipments of commercial raw linseed oil contain foots, frequently in excessive quantities, and the only recourse the paint manufacturer has is to settle his oil in tanks until it is substantially freed from foots, an operation which involves considerable expense and wastage. It is the experience of the author that paints containing appreciable quantities of foots very frequently give serious trouble when used where the service requirements are such as to necessitate the use of a strictly high grade paint.

**86. Estimation.** Two methods have been devised, one by Walker and Wertz and the other by the author, to determine the comparative amount of foots in linseed oil.

**87. Walker and Wertz method.** Prepare a solution of calcium chloride saturated at room temperature. To this add 10 per cent by volume of concentrated hydrochloric acid. Mix thoroughly 25 c.c. each of oil and acetone and 10 c.c. of the acid calcium chloride and pour into a graduated tube to settle. All should be at room temperature.

Pickard<sup>1</sup> in the following table (XIV) records the results obtained by applying this test to representative shipments of raw oil made by several oil producers, the other analytical constants being included as of interest in connection with the percentage of foots.

<sup>1</sup> Proceedings A. S. T. M., Vol. XVII, Part 1, page 380.

TABLE XIV

## 88. Analytical constants of raw linseed oil

NORTH AMERICAN SEED			
Specific Gravity at $\frac{15^{\circ}.5}{15^{\circ}.5}$ C.	Iodine Number	Acid Number	Foots, Per Cent
0.9345	186.9	2.0	3.2
0.9358	189.8	1.2	0.4
0.9342	187.9	1.4	0.4
0.9348	182.0	2.3	1.6
0.9345	186.9	0.8	2.0
0.9348	189.2	1.0	0.8
0.9338	187.5	2.2	0.4
0.9349	186.1	0.8	2.0
0.9340	185.7	2.0	4.0
0.9341	187.2	2.2	1.5
0.9347	187.2	2.0	1.2
0.9347	184.4	2.3	2.0
0.9346	184.8	2.3	1.2
0.9344	182.4	3.2	2.0
0.9343	183.4	4.0	2.8
0.9343	183.8	3.1	3.6
0.9346	184.5	1.8	1.0
0.9347	183.3	2.4	2.5
0.9346	185.2	2.4	1.6
0.9344	184.3	2.9	2.0
0.9342	184.4	2.1	1.6
0.9342	186.4	1.7	0.8
0.9343	185.3	0.9	0.4
0.9341	188.3	1.9	3.6
0.9340	185.7	1.7	1.6
0.9345	186.8	0.5	0.8
0.9346	186.6	1.1	1.6

## SOUTH AMERICAN SEED

0.9326	173.2	4.0	2.8
0.9326	176.1	2.6	3.2
0.9323	176.0	4.2	2.8
0.9327	175.6	4.0	3.6
0.9326	174.9	4.0	4.0
0.9318	175.3	2.1	2.4
0.9327	175.1	3.4	2.8
0.9322	176.5	2.1	4.0

89. Author's method. The method devised by the author<sup>1</sup> depends on the precipitation of the foots by shaking 100 c.c. of syrupy phosphoric acid and 100 c.c. oil, thinning with 150 c.c. naphtha and allow-

<sup>1</sup> Drugs, Oils and Paints, July, 1916, page 51.

ing the foots to collect in the calibrated neck of a suitable flask, keeping the temperature at approximately 30° C. during the operation.

Oils, fresh from the filter press, gave volume readings of 4 to 5 per cent; the same oils after settling for 3 months showed about 0.1 per cent foots. The author has examined commercial shipments having as high as 6 per cent foots.

**90. Composition of linseed oil foots.**<sup>1</sup> The foots from linseed oil, manufactured by the naphtha extraction process, after centrifuging, contained 75.8 per cent linseed oil, the extraction being conducted with carbon disulphide. The insoluble portion contained:

	Per cent
SiO <sub>2</sub> .....	34.38
CaO.....	7.98
MgO.....	8.39
P <sub>2</sub> O <sub>5</sub> .....	46.50
K <sub>2</sub> O.....	Present
	<hr/> 97.25

The foots from an hydraulic pressed linseed oil contained:

	Per cent
SiO <sub>2</sub> .....	None
CaO.....	3.26
MgO.....	4.99
K <sub>2</sub> O.....	10.27
P <sub>2</sub> O <sub>5</sub> .....	81.08
	<hr/> 99.60

<sup>1</sup> Eisenschymml, J. Ind. and Eng. Chem., January, 1910.



## CHAPTER VII

### LINSEED OIL (Continued)

**91. Determination of hexabromide number of linseed oil fatty acids.**<sup>1</sup> G. W. Thompson considers the method given below as very satisfactory for determining the purity of linseed oil. 0-29

The determination of the hexabromide number is preceded by the preparation of free fatty acids.

**92. Preparation of pure linseed oil fatty acids.** Three and one-half grams of the linseed oil are weighed into each of three round-bottom evaporating dishes of about 220 c.c. capacity. Then 45 c.c. of one-half-normal alcoholic potash are added in each case and the dishes are placed on the water bath. This is brought slowly to boiling. The oil is frequently stirred with a glass rod, flattened at the end. By this method, the saponification is better and more quickly accomplished.

The alcoholic potash is prepared as follows: 28 g. of solid pure caustic alkali are placed in a 1-liter measuring cylinder and dissolved in from 30 to 40 c.c. of distilled water; then 97 per cent ethyl alcohol is added, to make the volume 1 liter. The solution is allowed to stand for 2 or 3 days to settle out any cloudiness due to potassium carbonate. This potash solution is best kept in a brown bottle, stoppered with a rubber stopper.

The water bath is not warmed until the evaporating dishes are filled. The saponification process begins

<sup>1</sup> Eibner, Farben Zeitung, Nov. 23, 1912.

slowly and gradually, so that the alcoholic soap solution does not crawl up to the rim of the evaporating dishes, thereby causing losses. The contents of the dishes are evaporated to dryness, with constant stirring and breaking up of the nearly dry soaps. In this way, the alcohol is completely removed. This whole operation of saponification and evaporation will take from 1 to  $1\frac{1}{2}$  hours. The resulting product will be a light yellow, agreeable smelling soap powder. The soap which first comes to dryness is mixed with 50 c.c. of hot water and dissolved on the boiling water bath. This requires about 5 minutes. This soap solution is added to the soap which next comes to dryness, and the first evaporating dish is rinsed out with water. Finally, this solution is added to the soap which last comes to dryness. The whole soap solution is cooled off somewhat and poured into a 1-liter separatory funnel, graduated at 180 c.c. and 340 c.c. The volume of the soap solution must now amount to 180 c.c. and must not be any greater. The light yellow soap solution, which is absolutely clear in a warm state, is now cooled down to the temperature of tap water, whereby it becomes slightly cloudy. By the addition of 20 c.c. of five-normal sulphuric acid, the linseed fatty acids are freed, and float on top of the liquid. They have an agreeable, characteristic odor and are, in the beginning, precipitated in an opaque, white form. After a few seconds, the emulsion disappears. The acids then are plainly yellow. The contents of the separatory funnel are now thoroughly shaken with 140 c.c. of ether (second mark at 340 c.c.), during which operation the cock is opened at least once to avoid excessive pressure. After 5 minutes, the aqueous solution is drawn off as much as possible, the yellow ether

solution of fatty acids is gently rotated and allowed to stand for a minute. After this operation, a little more water will settle in the lower part of the separatory funnel, and is removed. After adding 70 g. of anhydrous Glauber's salt, the fatty-acid solution is allowed to stand overnight in the separatory funnel.

**93. Procedure.** The detailed operation is as follows: Saponification should not be started until the afternoon. After setting free the fatty acids with sulphuric acid, 100 c.c. of ether are first used for shaking out and allowed to stand. The aqueous solution is drawn off into a second separatory funnel, and then shaken out again with 40 c.c. of ether. The combined ether solutions of fatty acids are then to be further treated as mentioned above.

The next forenoon, the recovery of the pure fatty acids is undertaken. For this purpose, a tared Erlenmeyer flask of 200 c.c. capacity is used. The flask is stopped with a well-pressed, two-holed cork stopper. In one of the holes is inserted a 50-c.c. dropping funnel, which supports an ordinary small funnel. In the other hole is placed a glass tube of 0.5-cm. bore, bent at a right angle, and this is connected with a Liebig condenser.

The dried ether solution of fatty acids is now filtered through a dry, folded filter ( $d = 18.5$  cm.) into a 150-c.c. Jena Erlenmeyer flask and from there is poured into the dropping funnel. Then about 100 c.c. of this solution are run into the 200-c.c. flask and the water bath is slowly warmed to about  $70^{\circ}\text{C}$ . As the ether is distilled off, more of the solution is added, drop by drop. The distilled ether is used to extract the Glauber's salt in the separatory funnel, which has absorbed a considerable amount of fatty acids. This

is done six times, using from 100 to 120 c.c. of ether each time. The fifth extraction is, as a rule, entirely colorless. Finally, by means of an ether wash-bottle, the folded filter, the flask used to receive the filtrate, the small funnel, and the dropping funnel are rinsed off, in order to recover quantitatively the fatty acids adhering to them. After the largest part of the ether is distilled off, the water bath is brought to boiling, and a few more cubic centimeters of ether will then be distilled off.

The extraction of the Glauber's salt and the distilling off of the ether take about  $1\frac{1}{2}$  hours. Even after ether has ceased to distill over, the fatty acids still contain some of it. Next, the flame of the water bath is extinguished, the Liebig condenser and dropping funnel are removed, and a tight-fitting stopper, with gas inlet and outlet tubes, is inserted in the flask. The end of the former tube is placed 1 cm. above the surface of the fatty acids. The outlet tube is drawn out to a capillary to prevent the hydrogen gas, which circulates above the fatty acids, from escaping too quickly, and to force it to mix with the ether vapors before leaving the flask. The hydrogen is first purified by passing it through an alkaline lead salt solution and then through concentrated sulphuric acid. The flask is replaced on the water bath, which is kept boiling vigorously. In order to drive off the ether, two hours are required. From four to five gas bubbles per second should pass through the flask. Experiments made with carbon dioxide instead of hydrogen give the same results, but we prefer to use hydrogen. Next, the fatty acids are removed from the water bath, and, with a clean cloth, the hot flask is wiped off on the outside and inside around the top

of the neck; then, while warm, it is put in a vacuum desiccator. This is evacuated to a high degree and then left standing for at least 4 hours. By this means, the fatty acids, as a rule, become partly solid. They are then weighed very quickly and put in a vacuum as before. After 2 hours, the flask is again weighed as quickly as possible, the weights having previously been put on the balance. Finally, the desiccator with flask is once more evacuated, and left standing overnight. The next morning, the weight of the flask is checked.

**94. Preparation of the 10 per cent ether solution of fatty acids.** From the 9 to 10 g. of weighed linseed oil fatty acids, a 10 per cent ether solution is now made. Forty cubic centimeters of ether, dried over calcium chloride, are added to the fatty acids and carefully shaken until the latter are dissolved. This solution is poured quantitatively into an accurately graduated 100-c.c. glass-stoppered measuring cylinder, the graduation marks of which run halfway around the circumference of the cylinder, whereas those for every 10 c.c. run entirely around the cylinder. By means of an ether wash-bottle, the empty flask is washed with 20 c.c. of ether, well shaken, and this liquid also is poured into the cylinder. The flask is then rinsed again, and care is taken to wash off whatever ether solution has run down on the outside. Then the cylinder is filled up nearly to the 100-c.c. mark and shaken. The glass stopper is raised for a moment, and after a minute the cylinder is filled to the mark and thoroughly shaken once more. The lower meniscus is read.

**95. The Brominizing process.** By means of a standardized pipette, marked at the top and bottom,



20 c.c. of the freshly shaken fatty-acid solution are removed from the graduated cylinder and placed in a 100-c.c. Jena Erlenmeyer flask with not too narrow a neck. This 20 c.c. should contain from 1.9 to 2.0 g. of fatty acids. A cork stopper, with a groove cut in the side, is placed in the flask, and then the latter is put in a cooling mixture of a temperature not exceeding  $-10^{\circ}\text{C}$ . This mixture is prepared in a suitable vessel, such as a water bath, by mixing finely broken ice with the necessary quantity of salt, and thoroughly stirring the mixture with a strong glass rod. In winter, snow can be used. The cooling mixture must be so made that the flask can be easily moved in it. After leaving the ether solution in the cooling mixture for 10 minutes, it will have the desired temperature. In the meantime, 1 c.c. of commercial bromine is placed in the brominizing burette. A 10-c.c. burette, or even a smaller one, is the most suitable, but the glass cock must be well ground in, and the delivery point must be fine. Before brominizing, the flask containing the fatty-acid solution must be shaken slowly in the cooling mixture. Five-tenths cubic centimeter of bromine — half of the quantity to be used — is added in single drops, and then the other 0.5 c.c. of bromine, in double drops, keeping the flask cold throughout the operation by carefully shaking it in the cooling mixture. The detailed method of procedure is as follows: The cock of the burette is slowly opened, permitting a single drop of bromine to run down the side of the flask, thereby preventing loss by spattering. The cock of the burette is then closed, and the flask is shaken in the cooling mixture. After from 12 to 15 drops of bromine have been added in this manner, the hexabromide of linolenic acid generally begins to

precipitate in the form of a fine crystalline powder, which settles quickly. With every additional drop, the precipitate can be plainly seen to increase. After 0.5 c.c. of bromine has been added in single drops, which should take approximately 20 minutes, the other 0.5 c.c. is added in double drops in exactly the same manner. This will take 10 minutes, so that the entire brominizing process will consume 30 minutes. After cooling for 2 minutes longer, the flask is again shaken and then allowed to stand stoppered for 2 hours in the cooling mixture. Over the precipitate can be seen a reddish brown fluid, a proof of the excess of bromine in the reaction mixture. Quite frequently it is observed that some of the precipitate adheres to the sides of the flask, due perhaps to the intense cooling. This, however, cannot be avoided and does not influence the quantitative recovery of the precipitated hexabromide. The time for brominizing, 30 minutes, must be strictly adhered to and must not be shortened. The added bromine disappears almost immediately, until an excess has been added. During the 2-hours standing, the temperature may rise somewhat, but in order to avoid secondary reactions as far as possible, it should never exceed  $-5^{\circ}\text{C}$ . In the meantime, the washing ether is prepared. Five c.c. of ether are put in each of 5 test tubes, which are stoppered and set in the cooling mixture. For filtering, a Daniel filtering tube is used, which is provided with an asbestos pad, made as thin and uniform as possible. Two grams of Kahlbaum's asbestos, suspended in 500 c.c. of water, will be sufficient for a series of determinations. On top of the asbestos a perforated porcelain plate is placed, the diameter of which must be almost as large as the inside diameter of the filtering tube. The per-

forated plate has about 20 round openings, 2 mm. in diameter. One liter of distilled water is drawn slowly through the tube, and the latter, with its cover, is then dried for one hour at  $110^{\circ}\text{C.}$ , allowed to cool for an hour in the desiccator, and then weighed. In weighing, the tube is suspended by an aluminum wire. After the bromide precipitate has stood for 2 hours in the cooling mixture, it is filtered. The tared filtering tube is connected with a filtering flask, which, however, during the whole filtering process, is not connected with the pump. After making sure once more that the cooling mixture is at the proper temperature, the operator removes the flask containing the hexabromide and wipes it off with a dry cloth, without disturbing the precipitate. With the assistance of a glass rod, and without disturbing the precipitate, the mother-liquor is now carefully poured upon the filter and allowed to drain through completely. In the meantime, the precipitate is thoroughly shaken with the first 5-c.c. portion of washing ether and left to settle in the cooling mixture. The ether becomes reddish brown; the precipitate becomes lighter. Immediately after the mother-liquor has run through the filter, the washing liquid in the flask is poured upon the filter, care being taken, however, to retain all the precipitate in the flask. The filter must never become dry, as this would cause a considerable delay in filtering.

The precipitate is then thoroughly mixed with the second 5-c.c. portion of ether and brought, as completely as possible, upon the filter, immediately after the first portion of washing ether has drained through. The precipitate settles instantly, and above it is a yellow solution which filters easily.

The flask is then cleaned with a feather, using the

third 5-c.c. portion of ether. Next, the precipitate still remaining in the flask is stirred up and brought upon the filter immediately after the preceding washing liquid has drained through. Then, the precipitate on the filter is stirred with a glass rod and is thus freed as much as possible from the mother-liquor. At this point, the washing ether, filtering through, still has a yellowish color, but the precipitate is almost white. The flask is again cleansed with the feather, using the fourth portion of ether. The latter, which is then colorless and contains only a trace of precipitate, is also poured upon the filter in such a way as to rinse the rim of the filtering tube, up to which some of the mother-liquor has crawled during filtration. The precipitate on the filter is once more stirred up with the glass rod. The ether filtering through is now, in most cases, very faintly yellowish or colorless. Then the last 5-c.c. portion of ether is used to rinse the flask once more. The glass rod is now cleaned with the feather, and the entire contents of the flask are brought upon the filter and allowed to run through. Then, with the filtering tube half covered, the filtering flask is connected with the suction pump, and the latter is worked strongly for one minute. The hexabromide shrinks to a very nice white mass. Occasionally, cracks occur in the precipitate. A small quantity of a slightly yellowish fluid is drawn from the bromide by the suction process, and the lower part of the filtering tube often becomes somewhat clouded with a small amount of residue left after the washing ether has evaporated. The filtering tube is now removed from the filtering flask, wiped off outside, and heated in a drying oven for 2 hours at from 80 to 85° C. Then it is allowed to cool for 1 hour in the



desiccator and is weighed. It has often been observed that a hexabromide, which would be snow-white in color if dried at 80° C., becomes gray on the surface if dried at 100° C. During filtration, especially during the first half of it, the precipitate must never become dry. Should this happen before the hexabromide is thoroughly pure, it can hardly be washed out completely, as sticky substances, bromides of various compositions, which, once dried, are difficult to dissolve in ether, adhere to the original precipitate. Before drying, the precipitate must be white, inside and out. If it shows a yellow color anywhere, it will partially melt during the drying process and become gray on the surface. The weight will then be somewhat too high. The filtering, as a rule, takes from 10 to 15 minutes and should not, at all events, exceed 25 minutes. The condition of the asbestos greatly influences the period of filtration. The hexabromide number is obtained by calculating the weight of hexabromide per 100 g. of fatty acids.

**96. Modifications.** Thompson<sup>1</sup> has adopted the following modifications. The pure fatty acids were poured into small vials holding approximately 2.0 g. when full and tightly corked. In this way, the fatty acids can be preserved for a considerable period without appreciable change. To make the test, the contents of one of the vials were poured into a weighed Erlenmeyer flask of 100 c.c. capacity, flask and contents reweighed, and the fatty acids dissolved in 20 c.c. of ether. 1.9 to 2.0 was found to be a convenient quantity to work with.

After the flasks had stood in the freezing mixture at -10° C. for two hours, the filtering and washing were

<sup>1</sup> Am. Soc. Test. Mat., Vol. XV, page 233



carried out as follows: A small wash-bottle containing ether was placed in a separate freezing bath and the contents cooled to  $-10^{\circ}\text{C}$ . The tip of the bottle was made to deliver a very fine stream. The time required to deliver the proper amount of wash ether was determined by experiment and can be judged very closely.

The flask was removed from the freezing bath and the mother-liquor carefully decanted. The precipitate was then washed down with a fine stream of ether, using about 5 c.c., and the precipitate and wash ether shaken thoroughly and allowed to settle out in the freezing bath. This washing by decantation was repeated three times. The precipitate was then transferred to a Gooch crucible, and the flask was washed out with about 5 c.c. of ether. It is seldom that any precipitate will be found adhering to the flask, but if such is the case, it can be removed with an ordinary rubber policeman. The precipitate on the Gooch crucible was allowed to drain, using a gentle suction if necessary; but care should be taken to prevent the precipitate from becoming dry. Washing was continued on the Gooch crucible, stirring up the precipitate each time with a fine stream of ether, and allowing it to drain almost dry, until the wash ether appeared colorless. Strong suction was then applied and the precipitate freed from the liquid. The Gooch crucible was removed and placed in a steam bath which was held at  $80^{\circ}\text{C}$ . and dried for one hour. The liquid in the filtering flask will be found to be about 50 c.c., and should not exceed this amount.

In following out this method results have been obtained which agree closely with those reported by Eibner.

TABLE XV

97. Percentage of hexabromides<sup>1</sup>

No.	Source	Per Cent Hexabromides
1.....	From N. A. Seed	48.90
2.....	" " " "	48.57
3.....	" " " "	51.88
4.....	" S. A. Seed	48.59
5.....	" Bombay Seed	50.87

98. Boiled linseed oil. The American Society for Testing Materials adopted in 1915 the following standard specifications for boiled linseed oil from North American seed.

	Maximum	Minimum
Specific gravity at $\frac{15.5^{\circ}}{15.5^{\circ}}$ C.....	0.945	0.937
Acid number.....	8	..
Saponification number.....	195	189
Unsaponifiable matter.....	1.5	..
Refractive index at 25° C.....	1.484	1.479
Iodine number (Hanus).....	..	178
Ash, per cent.....	0.7	0.2
Manganese, per cent.....	..	0.03
Calcium, per cent.....	0.3	..
Lead, per cent.....	..	0.1

99. Effect of hydrolysis on the acid number.<sup>2</sup> Since the metallic linoleates and resinates are so easily hydrolyzed, it is apparent that their presence in the dissolved state would cause an oil or varnish to show an acid value, which would include the amount of alkali necessary to hydrolyze the soaps present as driers, as well as that required to neutralize the free fatty acids.

Lead, manganese, cobalt, and zinc linoleates hydrolyze completely during titration. Calcium linoleate

<sup>1</sup> Thompson, Proceedings A. S. T. M., Vol. XIII, page 378 (1913).

<sup>2</sup> Ware & Christman, J. Ind. and Eng. Chem., Vol. VIII, page 996 (1916).

hydrolyzes to the extent of 50 per cent. The rosin salts of the same metals hydrolyze as follows:

	Calculated Acid Value Assuming Complete Hy- drolysis	Apparent Acid Value	Per Cent Hydrolyzed
Lead salt.....	139.0	113	81.3
Manganese salt.....	171.2	168	98.3
Cobalt salt.....	170.3	160	94.0
Calcium salt.....	175.3	86	49.1
Zinc salt.....	168.7	149	88.3

To arrive at the true acid value of boiled oil, enamel liquid, or varnish, it is therefore necessary to deduct from the total amount of alkali used the amount required to hydrolyze the metallic soaps present.

**100. Grinding oils.** For grinding white lead and combination paste whites, specially prepared linseed oils are used, which have been largely freed from the coloring principles that would otherwise stain the paint yellow. These grinding oils are made to meet the various requirements of the paint grinder as to acid number, some having low acid values while others have acid numbers of from 12 to 16. The determination of the acid value is therefore of prime importance. The other constants will be found to correspond to those of raw linseed oil.

**101. Bodied linseed oils.** These oils may be divided into two classes, viz.:

Blown oils, prepared by blowing air through a moderately heated oil, which has been previously freed from foots, until the desired consistency has been obtained. These oils are characterized by a low acid number of about 6 to 7, very heavy body, a low iodine number and a tendency to become insoluble on standing after having been largely diluted with naphtha.

Heat bodied oils, prepared by heating a linseed oil

that has been freed from foots and so treated that it becomes nearly water-white when heated to about 600° F. The heating is continued at this temperature until the desired body has been obtained. Such oils have high acid values, varying from 15 to 30 or even higher according to the amount of heat they have received. The iodine value decreases rapidly as the body increases, and with very heavy oils may be less than 100. Such oils are used extensively in enamel liquids, certain varnishes and in reducing oils.

## CHAPTER VIII

### TUNG OIL (CHINESE WOOD OIL)

**102. Valuation.** The paint manufacturer is enabled to control the purity of his linseed oil by purchasing direct from the crusher; with tung oil he has no such assurance, as the oil will have passed through several hands before it reaches him. As this oil is frequently adulterated and as it requires only a small percentage of adulteration to seriously impair its value in varnishes, it is necessary that each shipment be carefully tested.

Because of the fact that a very small percentage of adulteration seriously affects the working qualities of tung oil, the ordinary chemical constants cannot be relied upon in determining its purity and suitability for use. Neither can the so-called heat or "gel" tests that are in common use be relied upon to detect adulteration. The author has tested numerous shipments that have been passed as pure by skilled operators using these standard tests, and he has found these shipments adulterated and unsuitable for use. The extremely unsatisfactory condition of the tung oil market during the winter of 1918-19, when large quantities of impure oil, which had nevertheless been certified as of satisfactory purity by various laboratories, were passing from one dealer to another in an effort to unload, thus causing a badly demoralized market, is ample confirmation of the above statements.



**103. Anomalous dispersion of tung oil.** The method, developed in the author's laboratory, has been found very satisfactory and has been used by him for valuing importations of tung oil for six successive years. This method is based on the phenomenon of the anomalous dispersion — inversion of the spectrum — exhibited by tung oil under certain conditions and its return to the normal position by the addition of a known percentage of another vegetable oil. Of all the oils examined by the author<sup>1</sup> tung oil, alone, exhibits a spectrum with the green at the top and red at the bottom, the other oils showing the characteristic spectrum, the red at the top and the green at the bottom. The addition of 15 to 25 per cent, depending upon the natural purity of the tung oil, of another vegetable oil, e.g., linseed, causes the spectrum to resume its normal position. The percentage of such added oil required to obtain a normal spectrum affords a direct numerical measure of the purity of the tung oil and is known as its turning point value.

**104. Constitution of tung oil.** Tung oil is composed essentially of the glycerides of elaeomargaric and oleic acids. The glyceride of oleic acid exhibits normal dispersion only and in admixture with the elaeomargaric glyceride acts solely as a diluent. Therefore the "turning point," i.e., the point when the dispersion ceases to be anomalous and becomes normal, depends on the amount of olein present in the oil.

Ware & Schumann,<sup>2</sup> from the results obtained by the potassium soap and light break methods, concluded that the percentage of elaeomargaric glyceride nor-

<sup>1</sup> Drugs, Oils and Paints, Vol. XXXI, No. 9, page 327.

<sup>2</sup> J. Ind. and Eng. Chem., 6 (1914), 806, 8.

mally present in tung oil varies from 90 to 94 per cent. One of the samples they reported on as containing 10 per cent olein was found by the author to have a turning point of 15.5, indicating that a tung oil composed of elaeomargaric glyceride only, would have a turning point of 25.5. That this assumption is approximately correct is evidenced by the fact that the author examined a sample of tung oil obtained direct from China having a turning point of 24.9 and a domestic sample obtained from nuts grown in Florida having a turning point of 25. Both samples had only a fraction of 1 per cent of oleic acid and its glyceride, olein.

**105. Procedure.** The method depends on the inversion of the spectrum, using a Pulfrich refractometer. The essential features of the apparatus are: a 90-degree Pulfrich prism (index of refraction 1.62) carrying a cell so mounted that the upper surface of the prism is above the level of the joining of the cell and prism; a powerful tungsten light as the source of the illumination; a slitted screen to eliminate the excess rays, and a telescope for observing the spectrum produced.

A weighed quantity, about 15 per cent, of pure linseed oil free from foots and moisture is added to the sample of tung oil to be tested, the mixture heated gently to not exceed 100° C., thoroughly stirred and cooled to 25° C. at which temperature the spectrum of the mixture is observed. Further weighed quantities of linseed may have to be added to cause the spectrum to resume its normal position, showing a distinct very narrow band of red along the upper edge of the spectrum. This being the most marked change and the one most readily observed, the descriptive term, "turning point," has been applied to it.

Further additions of linseed oil merely increase the distinctness of the red and cause the gradual appearance of the green, until finally the entire spectrum has been completely reversed to its normal position.

**106. Variation in the composition of tung oil.** The natural composition of tung oil is subject to variation from year to year, due presumably to climatic conditions. In no instance, however, has the author found a well authenticated shipment of tung oil of commercial purity to contain more than 10 per cent olein or have a turning point value of less than 15.5 at 25° C. Commercial shipments have been examined having a turning point value of 22, equivalent to approximately 3 per cent olein.

**107. Normal purity.** In judging the purity of tung oil, it is therefore necessary, first to establish the normal purity of the oil crop of the current year, taking into consideration that several months elapse from the time the nuts are harvested until the oil is received in this country.

Commercially acceptable shipments of tung oil for 1913, 1914, and 1915 gave a very uniform turning point value of 15.5 at 25° C.; in 1916 this value varied from 19 to 21, and in 1917 from 20 to 22, while in 1918 it dropped to 16 from 18. Tung oil of low acid number and having a turning point value of 15.5 has been found in actual practice to be satisfactory in all respects.

If the normal turning point value for the current year should be found to be 15.5 and a certain shipment gave a value of 10, the oil would be considered adulterated to the extent of 5.5 per cent.

**108. Acid value.** In actual practice the author has found that the higher the acid value, the turning point

value remaining constant, the slower will be the oil to acquire its "body" in the varnish kettle. Knowing both the turning point values and the acid number, the behavior in the varnish kettle of one tung oil compared with another can be very definitely determined, and therefore this method of examination is of direct value to the varnish maker in governing the treatment that the tung oil will receive.

The following table<sup>1</sup> gives the results from tung oils obtained direct from the primary Chinese merchants in the local districts where the 1916 oil crop was produced.

TABLE XVI

**109. Imported tung oils.**

Number	Acid Value	Turning Point Value 25° C.
1.....	7.3	23.6
2.....	2.5	20.5
3.....	3.7	23.9
4.....	7.6	22.3
5.....	1.4	24.9
6.....	6.6	22.5
Average.....	..	23.0

**110. Climatic influences.** The influence of climatic conditions as affecting the composition of tung oil is clearly shown in the accompanying table.<sup>2</sup> These domestic produced oils were obtained direct from the 1916 crop of nuts by the author, the meats being heated to 80° C. and subjected to hydraulic pressure.

<sup>1</sup> Drugs, Oils and Paints, Jan. 1917.

<sup>2</sup> Drugs, Oils and Paints, May, 1917.

TABLE XVII

## 111. Domestic tung oils.

No.	Source	Color	Specific Gravity 15.5° C.	T. P. Value 25° C.	Acid Value
1	Georgia Exp. Station. . . . .	Very Pale	.9408	23.4	0.49
2	Fairhope, Alabama. . . . .	" "	.9402	23.0	0.37
3	Ala. Board of Horticulture	" "	.9383	23.0	0.79
4	Tallahassee, Florida. . . . .	" "	.9402	25.0	0.60
5	Univ. of California. . . . .	" "	.9368	9.0	0.45
6	Riverside, California. . . . .	" "	.9365	8.0	0.50

Oils numbers 5 and 6 would be unsatisfactory for commercial usage and when examined by the method developed by the author, as well as by the procedure defined by the American Society for Testing Materials and also by practical test, would be considered as heavily adulterated.

*Standard Specifications for Purity of Raw Tung  
Oil Adopted by the American Society for  
Testing Materials (1916)*

**112. Properties.** Raw tung oil shall conform to the following requirements:

	Maximum	Minimum
Specific Gravity at $\frac{15.5^\circ}{15.5^\circ}$ C. . . . .	0.943	0.939
Acid Number. . . . .	6	..
Saponification Number. . . . .	195	190
Unaponifiable Matter, per cent. . . . .	0.75	..
Refractive Index at 25° C. . . . .	1.520	1.515
Iodine Number (Hübl, 18 hours). . . . .	..	165
Heating Test (Browne's Method), minutes	12	..
Iodine Jelly Test, minutes . . . . .	4	..

**113. Specific gravity.** Use a pycnometer accurately standardized and having a capacity of at least 25 c.c., or any other equally accurate method, making the test at 15.5° C., water being .1 at 15.5° C.



**114. Acid number.** Weigh 10 g. of oil in a 200-c.c. Erlenmeyer flask, add 50 c.c. of neutral alcohol, connect with a reflux air condenser (or place small funnel in neck of flask), and heat on a steam bath for  $\frac{1}{2}$  hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with N/5 sodium hydroxide. Calculate as the acid number (milligrams of potassium hydroxide to 1 g. oil).

**115. Saponification number.** Weigh from 2 to 3 g. of oil in a 200-c.c. Erlenmeyer flask, add 30 c.c. of N/2 alcoholic solution of potassium hydroxide, connect with a reflux condenser, heat on a steam bath for 1 hour, then titrate with N/2 sulphuric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cubic centimeters of acid required by the blanks and the determinations, calculate the saponification number (milligrams of potassium hydroxide to 1 g. of oil).

**116. Unsaponifiable matter.** To 25 g. of oil add 15 c.c. of an aqueous solution of KOH (200 g. of KOH dissolved in water and made up to 300 c.c.) and 35 c.c. of 95 per cent alcohol. Connect with a reflux condenser and heat on the water bath for 1 hour with occasional shaking. Transfer to a separatory funnel containing a little water and wash out flask with water, using in all 125 c.c. Cool, add 200 c.c. of ether and shake vigorously for 1 minute. In a few minutes the ether solution will separate perfectly clear. Draw off the soap solution into another separatory funnel. Shake the soap solution with three 100-c.c. portions of ether. Unite all the ether portions and wash with three 30-c.c. portions of water. Filter the ether solution (small portions at a time) into

a tared flask, distill off the ether and dry flask and contents to constant weight at 95 to 100° C. in a steam oven. Report the percentage of unsaponifiable matter.

0-28 **117. Refractive index.** Use a properly standardized Abbé refractometer at 25° C., or any other equally accurate instrument.

0-15 **118. Iodine Number (Hübl).** Place a small quantity of oil into a small weighing bottle or beaker. Weigh carefully. Transfer by dropping from 0.2 to 0.3 g. into a 500-c.c. bottle having a well-ground stopper, or a specially flanged neck, iodine-test Erlenmeyer flask. Reweigh the weighing bottle or beaker to determine the amount of oil used in the test. Then dissolve the oil in 10 c.c. of chloroform and add an amount of Hübl solution containing twice the amount of iodine that will be absorbed by the oil. Stopper the flask, shake well, and place in a dark closet for 18 hours. Add 20 c.c. of a 10 per cent solution of potassium iodide and 100 c.c. of distilled water. Titrate with N/10 sodium thiosulphate, using starch as an indicator. Blank tests must be made. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 g. of oil).

On account of the fact that Hübl solution after preparation is apt to deteriorate in strength, it is considered advisable to have prepared the two component parts of Hübl solution, namely, a solution of mercuric chloride in alcohol and a solution of iodine in alcohol, of the proper strength, as outlined in text-books. The proper amounts of these solutions may be mixed on the day of use.

**119. Heating test (Browne's method).** Test tubes for containing the oil should be 16 cm. by 15 mm., with a mark near the bottom to indicate 5 c.c., and closed by a cork so perforated that a glass rod 3 mm. in diameter can move freely.

Fill a copper beaker (height, 12 cm.; internal diameter, 6 cm.) with cotton-seed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath. 0-27

Use a nitrogen-filled immersed-stem chemical thermometer, engraved stem; total length 4 to  $4\frac{1}{2}$  in.; graduated from 210 to 310° C. in 2° intervals; the length between 210 and 310° C. not less than  $2\frac{1}{2}$  in. If preferred, use emergent-stem thermometer 30 cm. long, with graduations from 100 to 400° C., making correction for emergent stem according to the method outlined in Stem Correction Sheet No. 44 of the U. S. Bureau of Standards.

**120. Procedure.** When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 c.c. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time, remove the source of heat for about 45 seconds, and then re-apply. Before 2 minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the tung oil has been in the bath about 9 minutes, raise the glass rod at intervals of  $\frac{1}{2}$  minute, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds of fluidity, a good end determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample.

No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the cotton-seed oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

**121. Iodine jelly test.** In a wide-necked 200-c.c. Erlenmeyer flask, place 2.5 g. (weight correct to 1 mg.) of the oil. Add 10 c.c. of chloroform from a pipette and stopper the flask immediately. Carefully insert a small glass vial into the flask so that the vial stands upright. Into the vial from a pipette run 10 c.c. of a solution of iodine in chloroform, containing 0.035 to 0.036 g. of iodine per cubic centimeter. Place the flask in a bath containing water at 25 to 26° C. and allow it to stand there for a few minutes. Keep the flask stoppered, except when it is necessary to remove it to insert the vial and to add the iodine solution. Tilt and rotate the flask so that the vial is upset and the contents of the flask are thoroughly mixed, at the same time starting a stop watch. Keep the flask in the bath at 25° to 26° C. and at the

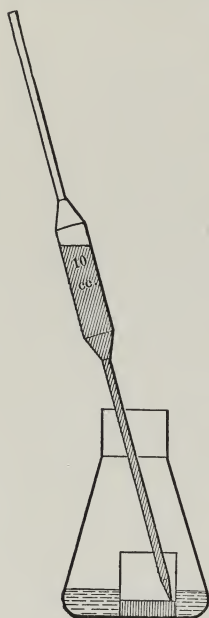


FIG. 5

end of every quarter minute, tilt the flask towards a horizontal position. Note the time required for the formation of a jelly that does not flow, but sticks to the bottom of the flask or slides as a mass. Record time in minutes and quarters thereof. Pure tung oil should require  $2\frac{3}{4}$  to  $3\frac{1}{4}$  minutes for the formation of the jelly. If the temperature of the laboratory is more than 2 or 3° C. above or below 25° C., place



the flask containing the iodine solution in the bath and allow it to remain there for several minutes before pipetting out the 10 c.c. for the test. The arrangement of the apparatus is shown in Fig. 5. The chloroform used to dissolve the oil and to prepare the iodine solution shall conform to the requirements of the United States Pharmacopoeia and shall have specific gravity at 25°/25° C. of not more than 1.481 and not less than 1.480. The proper density can be obtained by washing with water if the specific gravity is too low, or by adding 95 per cent ethyl alcohol if too high.

**122. Preparation of iodine solution.** A convenient procedure for preparing the iodine solution is as follows: Treat an excess of iodine with warm chloroform and after shaking for a few minutes, cool the contents to about 20° C. and filter through glass wool. Pipette 10 c.c. of the solution into a flask containing 10 c.c. of 10 per cent potassium-iodide solution and titrate with 0.1 normal sodium-thiosulphate solution. Calculate the iodine content and dilute with chloroform so as to obtain an iodine content of 0.035 to 0.036 g. per c.c. After dilution, titrate again against the thiosulphate to be sure that the solution is of required strength.

All the details of the above method shall be followed exactly.

**123. Regulations of New York Produce Exchange regarding purity of tung oil.**<sup>1</sup> "Pure China wood oil shall answer the accepted chemical requirements. The oil shall stand the heat test herewith subjoined."

*Heat test.* One hundred grams of the oil are heated in an open metal pan, 6 inches in diameter, as rapidly as possible, to a temperature of 540 degrees Fahrenheit.

<sup>1</sup> Rules New York Produce Exchange (effective July 1, 1918).



The time required to heat the oil from room temperature to 540 degrees should be, as nearly as possible, the same each time, four minutes being usually sufficient with gas burners. Hold the oil at or as near to 540 degrees as possible, stirring until it begins to solidify. Note the time required after the oil reaches 540 degrees, and until it begins to solidify. This should not exceed  $7\frac{1}{2}$  minutes for any commercially prime wood oil. When the oil has solidified in the pan, turn it out while still hot, and cut with a knife. Commercially prime wood oil gives a product that is pale, firm, and cuts under the knife like dry bread, not sticking. If the oil requires more than  $7\frac{1}{2}$  minutes after reaching 540 degrees until beginning to solidify, or if the product is dark, soft, or sticky, the oil may be rejected.

## CHAPTER IX

### MISCELLANEOUS PAINT AND VARNISH OILS

**124. Soya oil.** Due to the increasing demand for linseed oil and the scarcity of this article, paint and varnish manufacturers are being forced to seek a substitute for this important material. Of the oils commercially obtainable in sufficient quantities to meet the needs of these industries, soya oil has been found the most satisfactory and adaptable.

**125. Uses.** Soya oil has been used to a considerable extent without admixture with other oils in oil colors, paste and semi-paste paints. Generally it is used in conjunction with linseed oil with the proper driers and is to a limited extent a component of varnishes and enamel liquids. From the following table (XVIII) it is evident that the iodine value of soya oil is the only chemical constant that markedly differentiates it from linseed oil. The average iodine number (Hanus) obtained by the author over a three-year period was 131.5. The acid value varied from 2 to 5. The author has, however, observed samples which had acid values in excess of 8, the oils having a characteristic rancid odor and not being suitable as a paint vehicle.

Commercially, soya oil is obtainable as an extracted oil and as an expressed oil, and the author has not been able to find any difference in their value as a paint vehicle. For the manufacture of driers and varnishes, however, it is necessary to specify when purchasing that the oil shall not "break" when heated,

and such shipments should be tested accordingly by the chemist, particular pains being taken to secure an average sample as certain extracted soya oils contain an appreciable amount of sediment (foots) which settles much more rapidly than is the case with linseed oils.

In admixtures with linseed oil from North American seed containing 25 per cent or less of soya oil, the iodine number of the mixture will be in excess of 170 and, therefore, would not furnish conclusive evidence of adulteration. Such mixtures behave very similar to linseed oils from South American seed, as to drying and hardness of the resulting film.

TABLE XVIII

**126. Analytical constants of soya oil <sup>1</sup>**

Variety	Specific Gravity 15.5° C.	Saponifi- cation	Iodine Number Hanus
Ebony, av. of 7 oils.....	.926	193	126
Ito San, av. of 19 oils.....	.925	193	131
Haberlandt, av. of 8 oils.....	.925	193	129
Manchurian, av. of 33 oils.....	.925	193	127
Austin, av. of 2 oils.....	.924	192	127

**127. Fish oil (menhaden oil).** The fish oil used in the paint industry is the variety obtained from the menhaden fish. Menhaden oil in its raw or natural state is not suitable for paint manufacture due to its odor, which is not only objectionable during the application and drying, but for a long time afterwards. Its iodine number is very close to that of linseed oil, and when treated to remove its objectionable odor it can be used to advantage in many industrial paints in conjunction with linseed oil. An oil with as low an acid value as possible should be selected.

<sup>1</sup> Washburn, N. D. Ag. Exp. St. Bulletin No. 118.

**128. Detection.** Usually such mixtures, when strongly heated, will give off a characteristic fishy odor. In case of doubt the Eisenschymml test <sup>1</sup> may be used: One hundred drops of the oil are dissolved in 6 c.c. of a mixture containing equal parts of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown coloration remains. After 10 to 15 minutes the test tube is placed in a beaker containing boiling water. Linseed oil and other vegetable oils, such as China wood oil, cottonseed oil, corn oil, etc., will clear up completely within a few seconds, while fish oils will remain cloudy and precipitate an insoluble bromide at the bottom of the tube after a short time. With a little practice 5 per cent of fish oil is clearly recognizable.

In the case of boiled linseed oil it is necessary to remove the metallic constituents before adding the bromine. This is preferably done by shaking with a 10 per cent solution of nitric acid saturated with potassium nitrate.

TABLE XIX

**129. Analytical constants of commercial menhaden oils**

No	Variety	Specific Gravity 15.5° C.	Acid Value	Saponification	Iodine Number
1	Extra Bleached.....	.916	12.9	186	137
2	Pure Pressed.....	.925	8.4	199	170
3	Light Pressed.....	.924	24.0	203	163
4	Pressed.....	.925	8.6	199	170
5	Pressed.....	.927	9.6	202	170
6	Treated, Bodied.....	.972	4.6	199	92
7	" " .....	.964	2.7	183	71

**130. Lumbang oil.** This oil closely resembles tung oil in appearance and in its analytical constants, but

<sup>1</sup> J. Ind. and Eng. Chemistry, February, 1910.

has an entirely different chemical constitution as it does not polymerize with heat or exhibit anomalous dispersion. When subjected to heat, it turns dark, does not "body" readily and, as far as the author has been able to ascertain, has not found a definite place in the paint or varnish industries.

*Analysis of Cold Pressed Lumbang Oil*

Specific gravity.....	0.927
Acid value.....	1.3
Iodine number.....	16.2
Saponification number .....	192.3
Refractive index.....	1.475

**131. Perilla oil.** This oil, due to its superior drying qualities and the hardness of the resulting film, is finding an increasing use in enamels, varnishes, and technical paints. Gardner gives the following constants for perilla oil.

Specific gravity.....	.937
Acid value.....	4.3
Iodine number.....	193.3
Saponification number.....	193.4
Refractive index.....	1.4780

Perilla oil frequently has a much higher acid value than linseed oil; samples examined by the author have varied between the limits of 5 and 11. Perilla oil bleaches under heat and takes on "body" very similar to a linseed varnish oil. Its higher acid value apparently does not render it more active toward zinc oxide or other pigments which produce "livering."

**132. Reducing oils.** These oils usually contain 50 to 65 per cent of mineral spirits or naphtha and are largely used for reducing industrial paste or semi-paste paints to painting consistency. For such purposes, these oils have a recognized standing, especially in the railroad trade. When linseed oil commands an



abnormally high price, these oils are offered generally on the market as substitutes for linseed oil, usually with extravagant claims as to their value.

The nonvolatile portion of the better grades of reducing oils consists of heavily bodied linseed oil, or mixtures of such oil with treated fish oils or tung oil, either with or without a small percentage of rosin, usually 4 to 7 per cent. The cheaper grades contain a much larger percentage of rosin or mixtures of rosin with heavy mineral oil bases, which cannot be regarded as having a legitimate place in the paint industry.

The bodying of these oils may be accomplished by blowing with air at a moderate heat, by heat alone, or by combination with sulphur. If sulphur be used, the nonvolatile portion will contain from 5 to 8 per cent by weight of combined sulphur. The presence of sulphur and the amount present can be determined by following the method given in section 306.

## CHAPTER X

### SEPARATION OF VEHICLE FROM PIGMENT

**133. Preparation of sample.** If the sample be a liquid paint in the unbroken package, the brand, manufacturer, and guarantee, or other statements of importance appearing on the label, should be carefully recorded. The can should also be examined for any evidence of leakage, or any markings indicating the date of manufacture. On opening the package the unfilled portion should be measured by placing a straight edge across the top of the can and measuring with a ruler the distance downward to the surface of the oil. The gross weight of the package should also be recorded at this time.

**134. Condition of sample.** The clear oil portion should be carefully removed with the aid of a pipette or suction flask, and the surface of the paste portion remaining should be examined carefully for evidence of any granulation or precipitation of the drier constituents, which will often form a gummy layer on the surface of the paste. The older the sample the more pronounced the precipitation or granulation. The condition of the paste portion is readily ascertained with a steel spatula, and the degree of settling, hardening, and any separation of the coarser particles due to poor grinding should be noted.

**135. Obtaining a uniform sample.** The paste is then completely removed to a larger can, known as the mixing can, which should be kept solely for this

purpose, and stirred until smooth. The reserved oil portion is gradually added, with constant stirring, which should be continued until the analyst is thoroughly convinced that the sample is uniform in composition. The entire success of the analysis depends upon securing a uniform sample, and more analyses are incorrect because of carelessness in the preparation of the sample to be analyzed than from any other source.

**136. Weight.** The weight of the cleaned can subtracted from the gross weight gives the net weight of the sample. The can is then filled to the height occupied by the sample, as noted above, with water from a carefully graduated measure, thus giving the net volume of the paint. The can is then filled to the brim with a measured amount of water and the capacity of the can recorded.

**137. Separation of the pigment.** Much difficulty is often experienced in extracting the vehicle from the pigment, due to the fineness of the pigment particles and the ease with which they pass through the walls of the extraction tubes. This difficulty, however, may be avoided by the use of the apparatus illustrated herewith (Fig. 6). The extraction thimble, containing a filter folded cylindrically, is dried in the hot-water oven for thirty minutes, weighed, and 10 to 15 grams of the sample weighed into it, extracted with ether for 24 to 36 hours, dried, and

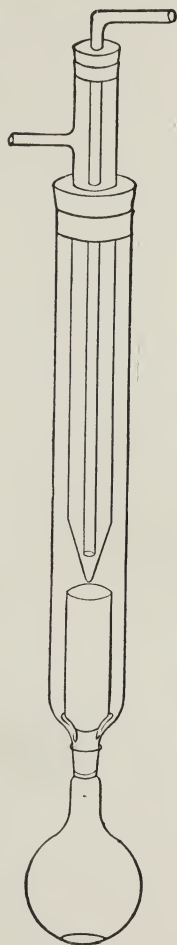


FIG. 6.  
EXTRACTION  
APPARATUS.

weighed again. The loss in weight represents the vehicle, and the residue remaining, the pigment, which is reduced to a fine powder and kept tightly stoppered until examined. Any casein or similar product in the paint will remain unextracted by the ether and unless detected will interfere with the proper analysis of the pigment. With very finely divided pigments, like Prussian blue, a thickly padded Gooch crucible may be used; the successive extractions may be decanted into it, using a strong suction and refilling the Gooch before it sucks dry.

**138. Extraction with acetone.** If the paint contains a considerable percentage of water the extraction can be best accomplished with the use of a good grade of acetone. Many chemists prefer a solvent prepared by mixing 50 parts benzol, 30 parts wood alcohol, and 20 parts refined acetone.

**139. Removal of vehicle in quantity.** Another method of obtaining sufficient vehicle from a liquid paint for the determination of the volatile oils, the quality of the linseed oil, etc., is to fill a tall cylinder with such of the sample as is not needed for the water estimation (100 to 150 grams) and for obtaining the free pigment, corking it tightly, and placing it in a tall copper can filled with water heated to about 70° C. By reducing the viscosity of the oil in this manner the pigment will settle quite rapidly, and in 24 hours, if the temperature is maintained at 70° C., sufficient oil may be siphoned off with aid of the suction pump.

**140. Use of centrifuge.** By far the most convenient method of obtaining sufficient vehicle for examination is by centrifuging the paint. In the average laboratory an electric centrifuge is the most convenient type. The cylinders used may be of glass,

but preferably of aluminum, as the pressure on the ends is often severe when the centrifuge is in motion. The bottoms of the cylinders should be removable,

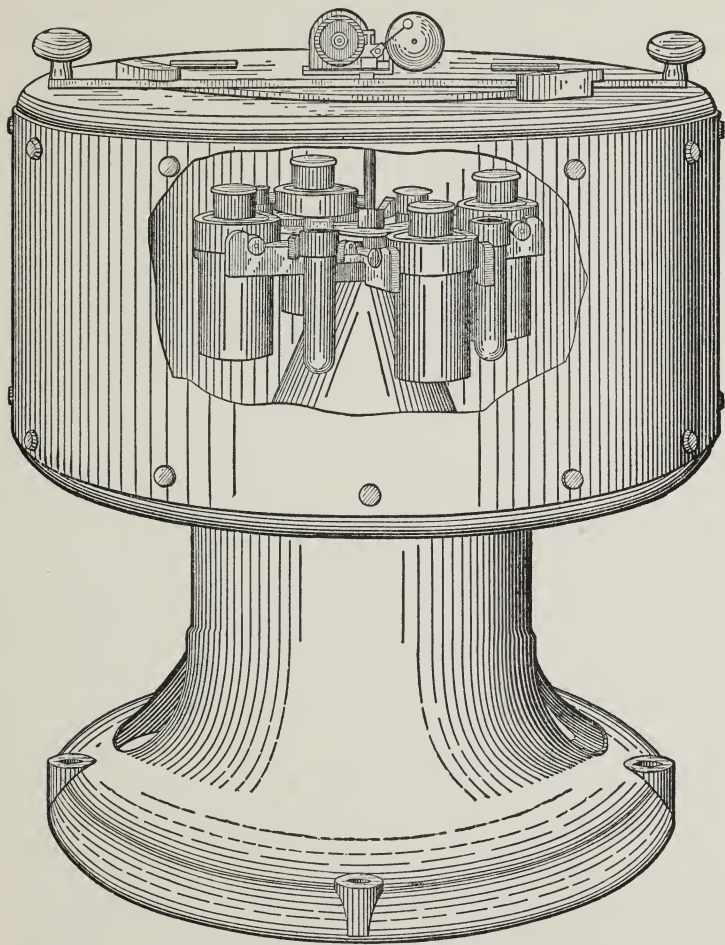


FIG. 7.

being screwed onto the cylinder. This permits of the easy removal of the precipitated paint and the rapid cleaning of the cylinders.



**141. Balancing the cylinders.** It is necessary that the cylinders opposite one another be evenly balanced, and it is always advisable to balance up the cylinders on the scales before placing them in the centrifuge. The cylinders should be tightly corked to prevent loss by evaporation of the volatile thinners, and live steam admitted into the centrifuge chamber sufficient to heat the contents of the tubes to about 70° C. In the majority of cases the pigment will be thrown out rapidly and cleanly and, by using a number of cylinders, an ample amount of the oils may be easily obtained.

**142. Power centrifuges.** In the factory laboratory, where the steam pressure is always available, an ordinary Babcock butter-fat tester can be conveniently used, the steam leakage into the upper chamber being sufficient to keep the tubes warm enough to insure the rapid precipitation of the pigment. The machine selected for this purpose should be very strongly made. One of the safest and most satisfactory centrifuges on the market is that illustrated in this connection (Fig. 7), manufactured by the International Instrument Company, Cambridge, Mass.

**143. Centrifugal force in centrifuges**

Centrifuge Head Rev. per Minute	Capacity of Tubes in C.c.	Average Rotating Diameter in Cm.	Force in Lbs. per Lb. in Revolutions per Minute					
8-place com- bination...	—	—	600	1200	1800	2400	3000	
	500	43	86	344	744	1380	2150	
	250	40	80	320	720	1280	2000	
	100	44	88	352	792	1480	2200	
	50	38	76	304	684	1216	1900	

**EXAMPLE:** A cup, weighing 2 pounds, at a speed of 3000 r.p.m., would exert a stress of 4000 lbs. on its trunnions.

**144. Cushioning of glassware.** A rubber cushion should be supplied for each tube. Place a little water in the metal tube, insert the glass tube, press down, and allow the water to overflow the metal tube. If this care is taken in the matter of balancing pressures and of cushioning there should be very little breakage of glassware.

**145. Rapid separation of pigment.** If only the pigment is desired the separated oil may be poured off and the precipitated pigment stirred up with benzine, centrifuged, and the operation repeated twice more. This will insure the removal of practically all the linseed oil, only a trace remaining. When dried the pigment should receive an especially careful mixing, as the centrifuging causes the pigments to settle to a certain extent according to their specific gravities.

**146. Separation of the oil for determination of its chemical constants.** The chief consideration in removing the oil for the determination of the iodine number, etc., is to prevent any oxidation of the oil during the recovery process, a necessity not fully appreciated by many commercial analysts. The vehicle obtained from the extraction described in section 137 is usually insufficient for this purpose, and the following procedure, used in many railroad laboratories, has been found very satisfactory.

**147. Procedure.** A quantity of the paint sufficient to yield about 30 c.c. of vehicle is weighed into one or more centrifuge bottles, and a sufficient quantity of redistilled petroleum ether (distilling under 60° C.) is added. Close the bottle tightly and shake until a uniform mixture is obtained. Centrifuge until a good separation is obtained. Pour, or siphon off, the clear supernatant solution on to a filter and into a round-

bottom distillation flask that will be about three-fourths full. Distill the greater portion of the petroleum ether, using an oil bath. Insert a steam distilling tube, raise the oil bath to  $120^{\circ}\text{C}$ . and pass a rapid current of steam until the volatile thinners are all over and at once pour the residual oil into a separatory funnel. Rinse out the flask with sulphuric ether (alcohol free), using a total of about 75 c.c. Shake and allow to stand until a sharp separation is obtained. Draw off the water, transfer the ether solution completely to a small flask, distill off the larger part of the ether, transfer again to a weighed beaker and drive off the remaining ether on a steam bath as rapidly as possible, being careful to prevent its foaming over. Cool immediately and weigh. Transfer to a small bottle of closely the same volume as the volume of the oil obtained, cork tightly and keep in a dark place until ready for further examination. It is practically necessary that the analyst constantly watches the final evaporation and notes the point at which the ether is completely gone, as further heating will rapidly lower the iodine value of the oil.

**148. Oxidation.** Boughton<sup>1</sup> found that portions of the oil extracted from a white lead paste heated for 2 hours at  $98^{\circ}$ – $99^{\circ}\text{C}$ . in air, in hydrogen and in carbon dioxide gave the following iodine numbers: 173, 182, and 180. Likewise a prepared linseed oil containing 3.23 per cent of lead in combination as linoleate, when heated at the same temperature for 2 hours and for 4 hours in air, gave 158 and 143 against 180 and 174 in carbon dioxide, the prepared oil itself having an iodine number of 177. A pure linseed oil having an iodine number of 179 was dis-

<sup>1</sup> J. Ind. and Eng. Chem., 5, 282.

solved in ether, the bulk of the ether removed by distillation, and the oil heated at 98°–99° C. gave the following results:

TABLE XX

Gas	Time	Iodine Number
Air.....	2 hrs.	174
Air.....	4 "	168
Hydrogen.....	2 "	177
Hydrogen.....	4 "	178
Carbon dioxide.....	4 "	179

**149. Total vehicle.** If the vehicle contains any considerable percentage of hard varnish resins, it will be advisable to use only sulphuric ether in the entire operation, in order to prevent the gums from precipitating.

The pigment remaining in the centrifuge bottles can be thoroughly stirred with more ether, until all lumps are broken up, and centrifuged again, repeating the operation until either three or four changes of ether have been used, as may be necessary. The ether is completely distilled off and the percentage of the residual oil plus the percentage of oil obtained in the first extraction is subtracted from 100, giving the percentage of pigment.

**150. Agricultural paste paints.** Paste paints containing para red are best extracted with petroleum ether, if the percentage of para color is to be determined in the extracted pigment. Frequently the darker shades of para reds contain soaps or sulphonated oils used to develop the color. When present, they will be extracted along with the vehicle when sulphuric ether is used, and also to some extent when petroleum ether is selected as the solvent. These soaps and oils slow up the drying of the vehicle to a very appreciable extent.

**151. Graining compounds and distemper colors.** The vehicle portion of these products is essentially water or a mixture of water and alcohol to prevent freezing in cold weather. A small percentage of dextrine or a similar binder may be present. The vehicle may be removed by distillation, using an oil bath, and the alcohol determined from the gravity of the distillate.



## CHAPTER XI

### ESTIMATION OF WATER IN PAINTS

**152. Occurrence.** A fraction of 1 per cent of water may occur normally in the vehicle. A small percentage, 1 to 3 per cent, may be incorporated into the paint by the manufacturer under the belief that it secures better penetration when applied to surfaces that are slightly damp, and also that it will prevent the pigment from settling and becoming hard in the can. Oftentimes, however, large quantities are introduced for the purpose of cheapening the product. The water may be added to the paint and prevented from separating out by forming an emulsion with the oil by the aid of an alkali or alkali salt, or by grinding it into the pigment, using an adhesive such as glue or casein. In the first case the nature of the ash left on burning some of the separated vehicle will indicate whether an alkali has been used or not. In the second case the vehicle will yield less than 1 per cent of water when distilled with a dry, inert substance, such as sublimed lead, as the water remains with the pigment.

**153. Conclusions.** Analytical results showing the presence of water in a paint product, even in considerable quantity, is not proof positive that the water was added intentionally as such. Many pigments carry considerable hygroscopic moisture. The author has analyzed shipments of leaded zincs in which the moisture content varied from 0.08 per cent to 1.68 per cent in the same shipment; ultramarine blues

were found to contain as high as 2.37 per cent moisture; ochers and raw siennas as much as 3 per cent and China clays as high as 6 per cent. Unless ground very hot in the paint mills, the hygroscopic moisture present in the pigments used will be found in the ground product and, if high, will in many instances, especially when varnishes are used, cause serious trouble from livering. The paint chemist should watch incoming shipments which are hygroscopic in nature and carefully check the percentage of moisture present.

**154. Presence of water in containers.** Recently there have been numerous complaints on the part of paint and varnish manufacturers regarding water in shipments of naphtha, both tank cars and drums, presumably due to the carelessness of the refiners in not properly cleaning the tanks and drums before re-filling. As these containers are usually emptied by drawing from the bottom, there is appreciable danger that the water will find its way into paint and varnish products. In the latter case there is serious danger from fire and injury to the workmen.

**155. Combined water.** Several pigments contain combined water which is easily split off when subjected to even moderate heat, and an analysis of a paint containing these pigments might indicate the presence of uncombined water when in fact the water was not present in the paint as such. Prussian and Chinese blues examined by the author have been found to contain 2 to 6 per cent of combined water, white lead 2 to 3 per cent, gypsum 19 to 21 per cent. Therefore the chemist in making analyses of paints containing these pigments should be especially careful as to reporting the presence of water.

**156. Determination of water with amyl reagent.**

This method has been found exceedingly satisfactory by the author and much more accurate than the distillation with toluene. The components of the amyl reagent — amyl acetate and amyl valerianate — must be free from amyl alcohol and other water soluble impurities. Fritsche Brothers, New York City, have furnished the most satisfactory article the author has been able to obtain. Each component should be washed with at least two changes of distilled water, which can be readily accomplished in a large separatory funnel and then redistilled, rejecting the first 20 per cent of the distillate. The reagent is obtained by mixing 5 volumes of the purified amyl acetate with 1 volume of the purified amyl valerianate.

**157. Procedure.** About 100 grams of the thoroughly stirred sample of paint are weighed into a flat-bottomed 200–250-c.c. side-necked distilling flask. Add 75 c.c. of the amyl reagent and with a gentle rotary motion secure a thorough mixing of the contents of the flask. Connect with an upright condenser and distill over about 60 c.c. of the reagent into a cylinder graduated into tenths of cubic centimeters. When the larger portion of water has passed over, the upper portion of the flask should be warmed gently with the naked flame, in order to expel the small portion of moisture that will have collected on the sides of the flask. The distillation should then be continued until the requisite amount of reagent has distilled over. The percentage of water can then be easily read off from the graduated cylinder and the contents of the distilling flask will be sufficiently liquid to insure easy removal. With paints high in volatile oils the volume of the distillate should be increased to at least 75 c.c.

A half-pint or pint varnish can heated in an oil bath is preferable to a glass distilling flask, as the danger of breakage is eliminated and the can may be discarded when the distillation is completed. Several hundred analyses made by this method on pulp leads and paste paints show that the combined water in white lead is not split off, that Prussian blue gives off practically all its water of combination and gypsum yields about 75 per cent of the water of crystallization present.

## CHAPTER XII

### WATER EMULSIONS AND EMULSIFIERS

**158.** Occasionally it devolves upon the paint chemist to determine the agents used for securing and maintaining the emulsion of oil and water in paints and for preventing the hardening of paste goods, such as combination leads, etc.

**159. Necessity of an emulsion.** The use of water in paints has been a much discussed question. The majority of paint manufacturers have maintained that the addition of a certain amount of water is essential for the preparation of a high grade paint, in order to prevent the pigments from settling hard in the bottom of the can, in which case there is much trouble and difficulty experienced in "breaking up" the paint when desired for use. As regards this contention the author believes the manufacturers are in the right, that better results are secured by the use of a small percentage of water in a paint high in lead and zinc. The line of demarcation, however, between the amount that can be considered legitimate for this purpose and that which may be considered as added for adulteration or cheapening, is by no means well defined. The author's experience has led him to believe that the true purpose of the addition of the water is best served by using an amount not exceeding 3 per cent of the vehicle present, and that any amount in excess of 5 per cent may be regarded as having been added for cheapening the product.



**160. Impairment of service value.** The addition of any considerable percentage of water unquestionably reduces the service value of a paint; but it is more often the materials used with the water to obtain the emulsion that cause the greater harm. Any substance which is astringent in its action, or which will cause a partial saponification of the oil, or bring about reactions between the oil and the pigments present, materially reduces the wearing value of such paint and the author can only regard the addition of such substances as willful adulteration.

Strongly emulsified paints, especially the cheaper grades, work a further deception on the consumer, unless he is advised as to what quality he is purchasing, in that such paints do not cover nearly as large areas per gallon as does a representative high quality paint, and therefore the economy is more apparent than real in the purchase of such emulsion paints.

**161. Deterioration.** Most emulsion paints, i.e., those containing over 5 per cent of water, will not keep in a usable condition when submitted to storage for a considerable interval of time. Certain reactions take place between the vehicle and the pigment which cause a gradual thickening of the paint, until in many instances all traces of the vehicle have apparently disappeared. The chemical actions set up and their cause are discussed in a subsequent chapter.

**162. Classification.** We may divide the emulsifying agents into two classes, — those which are inert and those which are more or less active.

The first class comprises such substances as:

Glue

Casein (containing no free alkali)

Oleates of lead and alumina  
Stearate of alumina  
Turpentine  
Alcohol  
Glycerine  
Starch

The second class:

Chloride of lime  
Sulphate of zinc  
Silicate of soda  
Carbonate of soda  
Caustic soda  
Lead acetate  
Borax  
Phosphate of soda

**163. Glue and casein.** The presence of glue and casein may be detected by heating a small portion of the pigment, secured by extraction with ether, in a small porcelain crucible and noting the odor given off, and comparing the same with that obtained by heating a mixed pigment to which a little glue or casein has been added. The amount present may be determined by running a nitrogen determination according to the Kjeldahl method and multiplying the nitrogen content by 6.37. About 10 grams of pigment should be used.

**164. Oleates and stearates of lead and alumina.** Oleate of lead is but rarely used, while the use of stearate is quite common. The present methods for detection and estimation are unsatisfactory, as paints containing white lead carbonate, sulphate or red lead, form lead soaps on standing with the linseed oil, which cannot be readily separated from the added soaps.

Stearate of alumina is frequently used, being present in solution in the vehicle. A quantitative estimation of the amount of alumina present in the ash obtained from incinerating the vehicle is presumptive evidence of the presence of a fatty-acid salt of alumina. Stearate of alumina is frequently found in flat wall finishes.

**165. Turpentine.** Turpentine is by far the best emulsifier to use, as it is, itself, a normal constituent of paint. The formation of a water-turpentine emulsion can best be accomplished by mixing into a paste a nonsettling pigment like asbestine (magnesium silicate) or China clay with a little linseed oil, adding water and turpentine. The following affords a base of uniform consistency and composition which can be added to any mix of pigments in any desired proportion:

150 lbs. China clay,  
150 lbs. asbestine pulp,  
21 gals. water,  
4 gals. linseed oil,  
2 gals. turpentine.

A formula like the above possesses much merit, as both China clay and asbestine pulp are especially valued for their nonsettling qualities, and acting in conjunction with the water will prevent any reasonable combination of pigments from settling hard, even when used in small quantity.

**166. Glycerine.** Glycerine and starch are often used in conjunction with each other, not only for the purpose of introducing water but to prevent the hardening of paste goods, such as combination leads. The following working formula illustrates their use:

500 lbs. white lead,  
300 lbs. zinc oxide "xx,"

150 lbs. white mineral primer,  
200 lbs. barytes,  
 $\frac{1}{2}$  oz. ultramarine blue,  
 $\frac{3}{4}$  lb. glycerine,  
1 lb. starch (powdered),  
15 $\frac{1}{2}$  gals. linseed oil.

Glycerine is also used in admixture with denatured alcohol and water to prevent settling and hardening.

**167. Chloride of lime and sulphate of zinc.** These products, while powerful emulsifying agents, are the most harmful to use owing to their astringent action on linseed oil. Just what the chemical reactions are which they enter into are difficult to determine, and it is difficult if not impossible to prove their presence in the majority of paints in which they are used, except as may be indicated by failure to give satisfactory service value.

**168. Carbonate of soda and caustic soda.** These two substances are perhaps more generally used than any of the others. The conversion of a portion of the linseed oil into a water-soluble soap necessarily results in decreasing the life, or wearing value, of the paint in which the above ingredients may be used. Their presence may be judged by incinerating a small portion of the vehicle and examining the nature of the ash obtained.

**169. Acetate of lead.** The use of acetate of lead as an emulsifying agent cannot be commended. It acts on the oil, although its effect is probably not so severe if it is incorporated into the paint subsequent to its passage through the mill as it would be if it were added in the original mix. A warm mill running under a suitable tension will cause any appreciable

amount of acetate of lead to act vigorously on the linseed oil, causing a more or less pronounced hardening in the package.

**170. Borax and phosphate of soda.** These products are usually used with carbonate of soda or caustic soda.

The following is a much used formula:

Phosphate of soda.....	6 lbs.
Bicarbonate of soda.....	6 lbs.
Water.....	40 gals.

Both of these substances can be detected by the well-known qualitative tests.



## CHAPTER XIII

### DETERMINATION OF VOLATILE THINNER

N-34

**171. Definition.**<sup>1</sup> The American Society for Testing Materials has defined "volatile thinner" as "all that liquid portion of a paint, water excepted, which is volatile in a current of steam at atmospheric pressure." The accurate determination of the volatile thinner in a paint, enamel, or varnish presents difficulties that are not readily apparent or indicated by the above official definition.

Linseed oil always contains a varying quantity of free fatty acids which are very appreciably volatile with steam at 130°–140° C. In a specification pure linseed oil semi-paste paint the author has found as high as 2 per cent volatile thinner which on examination was found to be composed of fatty acids from the oil used. A heat bodied linseed oil having an acid value of 24 to 30, such as is frequently used in enamel liquids and varnishes, contains a proportionately larger percentage of volatile fatty acids than raw linseed oil. Damar gums also contain 1 to 2 per cent of oil, volatile at 130° C.

**172. Increased use of heavy naphthas.** As long as the paint and varnish industries confined their requirements for volatile thinners to gum spirits of turpentine and to the established grades of P. and V. M. naphthas, distillation with steam at 100° C. could be relied upon to remove all of the volatile thinner pres-

<sup>1</sup> A. S. T. M. Standards, 1918, page 748.

ent, unless the product was a paste, semi-paste or short oil varnish, in which case an appreciable percentage of volatile thinner was retained in the product examined, due to heavy consistency of the mass.

The above mentioned thinners have been largely replaced by heavy naphthas, which evaporate much more slowly, as they contain a considerable percentage of hydrocarbons distilling above 200° C. These high boiling point fractions are volatile with steam at 100° C. only under prolonged treatment, and if the residual mass is gummy or pasty a considerable percentage will remain unvolatilized, causing a very appreciable error in the determination. Distillation by direct heat requires a temperature sufficiently high to produce decomposition products in sufficient quantities to cause serious error and contaminate the distillate obtained.

**173. Procedure developed by the author.** To meet the above mentioned difficulties the author has developed the following procedure. A weighed quantity of the product to be examined, containing approximately 100 c.c. of vehicle, is weighed by difference into a one-half-gallon varnish can, or other suitable container, and about 75 g. paraffine wax (m.p. 125°–130° F.) added, the function of the wax being to keep the mass in a freely fluid condition during the entire volatilization of the thinner. The can is immersed for about two-thirds its height in an oil bath, kept between the limits of 130° C. and 135° C. The can is provided with a steam-distilling tube extending to the bottom and a suitable source of live steam. A distilling bulb is used having an additional opening in the lower part of the stem and also an extra opening near the top of the inner tube in the bulb, to pre-

vent drops of the vehicle which may collect in the stem or bulb from being carried over mechanically with the distillate. The distilling bulb is connected with a vertical coil condenser discharging into a partially filled 100-c.c. burette with a rubber tube connection serving as a siphon overflow, thus permitting the aqueous distillate to pass continuously into a 16-oz. graduate.

To completely remove all of the volatile thinner it is usually necessary to continue the distillation until 32 oz. of aqueous distillate have been collected. This aqueous distillate will carry with it a slight quantity of the volatile thinner, and considering the large volume of the former as compared with the latter, the error arising from this cause is often considerable. It, however, becomes negligible, if the aqueous distillate from a previous determination of volatile thinner be used for generating the steam.

The volume of thinner is noted, after the adhering drops of water on the wall of the burette have been dislodged with a stiff wire. The gravity, distillation and polymerization can be determined in the usual manner. If however the nonvolatile vehicle contains a considerable percentage of linseed oil, it will be advisable to redistil the thinner to free it from the fatty acids before subjecting it to the polymerization test.

**174. Aromatic hydrocarbons and olefins.** The percentage of benzole and its homologues can be determined by the following method.<sup>1</sup> A mixture of 80 volumes of concentrated sulphuric acid and 20 volumes of fuming sulphuric acid is prepared, and 25 c.c. of the sample and 25 c.c. of the mixture are shaken vigor-

<sup>1</sup> Kramer and Bottcher, *Gewerbebeiss*, 1887.

ously for 15 minutes in a 100-c.c. flask with a suitably graduated neck. After 30 minutes, concentrated sulphuric acid (not the mixture) is added until the oily residue can be measured in the neck. The volume of unattacked hydrocarbons is read after standing for an hour, or when the volume no longer increases. Allowance should be made for the average percentage of hydrocarbons in petroleum thinners that react with the acid, as described in Chapter XVII, Comparative Analysis of Black Baking Japans. If extreme accuracy is required the procedure developed by Thole may be followed. *Journal Soc. Chem. Industry*, Vol. 38, No. 4, p. 39.

**175. Results.** The following table (XXI) gives the results obtained in the author's laboratory with various volatile thinners. The mineral spirits used conformed to government specifications but came just within the upper limits as to distillation and residue on evaporation. The amount used in each case was a known quantity and due precautions were taken to avoid loss prior to the distillation. Sixty grams of paraffine wax (m.p. 130° F.) were used as the diluent in each determination.

Tests made with the ordinary types of distilling bulbs show that 1 to 4 per cent of the nonvolatile vehicle is carried over mechanically with the volatile thinner in paint products containing a large percentage of linseed oil.

TABLE XXI

**176. Recovery of volatile thinners**

C.c. volatile thinner recovered with each 8 oz. aqueous distillate

Material	1st 8 oz.	2d 8 oz.	3d 8 oz.	4th 8 oz.	Total c.c. volatile obtained	Total c.c. volatile present
Hardened Rosin . . . . .	...	...	...	...	0.0	0.0
Treated Tung Oil (100 g.)	...	...	...	...	0.3	0.0
Treated Tung Oil, Mineral Spirits . . . . .	62.0	2.4	0.7	0.4	65.5	...
Treated Linseed Oil . . .	0.4	0.2	0.1	0.1	0.8	0.0
Raw Oil, av. of 5 shipments . . . . .	0.3	0.2	0.2	0.0	0.7	0.0
Reducing Oil (L. O. and M. Spts.) . . . . .	60.3	2.7	0.7	0.7	64.4	64.8
Varnish (Rosin and Mineral Spts.) . . . . .	59.8	2.3	0.9	0.6	63.6	63.4
Varnish (Rosin, T. O. and M. Spts.) . . . . .	40.3	2.0	0.8	0.4	43.5	43.5
Varnish (Rosin, L. O. and M. Spts.) . . . . .	62.3	3.4	1.2	0.6	67.5	67.6
B. Damar (100 g.) . . .	...	...	...	...	1.2	0.0
Varnish (B. Damar and Mineral Spts.) . . . . .	...	...	...	...	62.9	62.2
Drier (Rosin, L. O. and M. Spts. $\frac{1}{2}$ & Turp. $\frac{1}{2}$ ) . . . . .	61.1	1.6	0.5	0.0	63.2	63.4
Varnish (Rosin, L. O. and Turp.) . . . . .	55.7	0.5	0.1	0.1	58.4	58.8
Varnish (Ros., L. O., M. Spts. $\frac{1}{2}$ and Kerosene $\frac{1}{2}$ )	54.3	5.0	2.0	0.7	63.0	63.2

**177. Loss of volatile thinner in grinding enamel pastes, coach and Japan colors.** That a considerable percentage of the volatile thinner is lost through evaporation in grinding pigments in varnishes, Japans, reducing oils, etc., is well known, but the full extent of this loss is not generally appreciated. The actual loss may however be easily determined by use of the following formula:

$X$  = Amount of loss of volatile thinner in pounds.

$Y$  = Number of gallons of finished product.

$P$  = Total weight of pigments used.

$V$  = Total weight of vehicle used.



$W$  = Weight of volatile thinner present per gallon.

$T$  = Theoretical yield of formula in gallons, calculated from the displacement of the pigments.

$B$  = Theoretical weight of paste per gallon.

$A$  = Actual weight of paste obtained per gallon.

$$B = \frac{P + V}{T}$$

$$A = \frac{P + (V - x)}{y}$$

$$y = \left( \frac{T - x}{W} \right)$$

$$Ay = P + V - x$$

$$x = P + V - A \left( \frac{T - x}{W} \right)$$

$$x = W \left( \frac{P + V - AT}{W - A} \right)$$

#### EXAMPLE

Total weight of pigments used... 500 lbs.

Total weight of vehicle used..... 204 lbs.

Weight of volatile thinner per  
gallon..... 6.5 lbs.

Theoretical weight of paste calculated from the displacement of  
the pigments..... 18.5 lbs. per gallon

Actual weight of paste obtained.. 21.8 lbs. per gallon

Theoretical yield..... 38 gallons

$$x = 6.5 \left( \frac{500 + 204 - 21.8 \times 38}{6.5 - 21.8} \right)$$

$$x = \frac{6.5(-124.4)}{-15.3} = 52.5 \text{ lbs. or } 7.5\% \text{ loss by weight.}$$

$$\frac{52.85}{6.5} = 8.13 \text{ gallons loss, or } 21.39\% \text{ loss by volume.}$$

**178. Loss of volatile thinner in ageing varnish.** In tanking varnishes, driers, reducing oil, etc., a slow but steady shrinkage in volume takes place, due to evaporation of the volatile solvent. The rate at which this occurs depends not only on the thinner but the conditions under which the vehicle in question is stored. The following examples indicate what may be expected under ordinary conditions of storage.

	Volatile in freshly made varnish	Volatile 3 mo.	Volatile 6 mo.
Rubbing Varnish . . . . .	48.0%	47.1%	46.1%
Grinding Japan . . . . .	55.0	....	47.0
Gloss Oil . . . . .	46.0	....	40.0
Damar . . . . .	47.0	43.0	41.0
Spar Varnish . . . . .	48.0	46.0	45.0
Short Oil Varnish . . . . .	54.0	50.0	47.0

**179. Specification paints and enamels.** In making paints, enamel and varnish products under definite specifications or to conform strictly to a label analysis, it is very necessary to take into consideration and make due compensation for losses of volatile thinner both in the grinding and thinning, as well as for evaporation losses during the tankage of the vehicles used.

## CHAPTER XIV

### EXAMINATION OF THE EXTRACTED OIL

**180. Specific gravity.** If the extraction of the oil has been carried out as described in Chapter X without oxidation, the oil, if pure linseed oil, will come within the accepted limits of specific gravity as given in the chapter devoted to linseed oil, unless the paint is old and reactions have taken place between the pigments and the oil, which are discussed at length in Chapter XV. When only a small quantity of the oil is available, a Westphal balance should be used in determining the gravity.

A low specific gravity may indicate

- (a) Mineral oils
- (b) Cottonseed oil
- (c) Corn oil
- (d) Soya bean oil.

A high specific gravity may indicate

- (a) Rosin or resinous products
- (b) Rosin oil
- (c) Treated tung oil
- (d) Bodied oils, —linseed, soya or menhaden, usually accompanied with considerable percentages of volatile thinner or heavy mineral oil.

**181. Iodine number.** If the original vehicle contains no volatile thinners, the iodine number, in connection with the specific gravity, will indicate the

character of the oil present. The determination should be made as described in Chapter VI.

**182. Determination of the free fatty acids.** Ten grams of oil are weighed into a suitable sized Erlenmeyer flask and 50 c.c. of neutral aldehyde-free alcohol added. The mixture is heated to about 60° C. for a minute or two, then cooled and titrated with tenth-normal alcoholic potash, using phenolphthalein as an indicator.

Oil made from moldy seed, or seed contaminated with mustard oil, or oil containing rosin or rosin oil, will have a high acid figure. Pure raw oil should have a low acid figure; boiled oil will have a slightly higher figure. Oils which have been in contact with the pigment for a considerable length of time, especially if water is present, will show a very high acid value. See chapter devoted to the Effect of Storage on Composition of Paints.

**183. Preparation of aldehyde-free alcohol for alcoholic potash solution.** Dissolve 1.5 grams of silver nitrate in about 3 c.c. of water and add to a liter of alcohol in a glass-stoppered cylinder, mixing thoroughly. Dissolve 3 grams of pure potassium hydroxide in 10 to 15 c.c. of warm alcohol. Cool, pour slowly into the alcoholic silver nitrate solution, without shaking. The silver oxide is precipitated in a finely divided condition. Allow to stand until the precipitate has completely settled. Siphon off the clear liquid and distill. The distillate will be neutral and free from aldehydes, and will not darken when used as a solvent for potash.

**184. Free mineral acid.** Any free mineral acid in bleached oil is determined by washing a definite weight of oil with water, separating the water, and titrating

the dissolved mineral acid present. Any mineral acid found will usually be sulphuric acid. Its presence is decidedly objectionable.

**185. Determination of the flash point of linseed oil.** For exact flash-point figures rather expensive and complicated testers are needed, but for commercial tests that yield approximately the same figures a very simple apparatus may be used, consisting of a two-ounce crucible, a thermometer reading at least  $300^{\circ}\text{C}$ ., and a small gas jet attached to a rubber tube, a flame about the size of a pea being used. The cup is filled two-thirds full of oil, the bulb of the thermometer suspended in it, and the oil slowly heated. The determination should be carried on in a place entirely free from drafts. At short intervals the gas flame is brought close to, but without touching, the surface of the oil, with a slow, sweeping motion. The first distinct puff of pale-blue flame that shoots across the surface of the oil indicates the flash point of the oil, and the temperature at which this occurs is noted.

**186. Conclusions.** Hurst states that linseed oil, whether raw or boiled, flashes at about  $243^{\circ}\text{C}$ ., but this figure is considerably lower than those obtained in this laboratory, the raw oils flashing in the vicinity of  $300^{\circ}\text{C}$ . and the pure boiled oils from  $275^{\circ}$  to  $300^{\circ}\text{C}$ . Volatile oils used in the drier added to the oil lower the flash point considerably, 4 to 5 per cent of volatile oil lowering the flash point to about  $250^{\circ}\text{C}$ . The other vegetable oils, as corn and cottonseed oils, flash at nearly the same temperature as linseed oil. Mineral oils, such as would be used for adulteration, flash at  $193^{\circ}$  to  $216^{\circ}\text{C}$ ., rosin oils at  $140^{\circ}$  to  $167^{\circ}\text{C}$ . The presence of rosin oil would also be indicated by the strong odor of rosin given off during the heating.



Naphtha and turpentine when present in linseed oil rapidly lower the flash point according to the percentage present, having a flash point themselves but little above that of room temperature.

**187. Correction to be applied to the thermometer reading.**

Let  $N$  = length of exposed thread of mercury expressed in degrees.

$T$  = observed boiling point.

$i$  = temperature of the auxiliary thermometer, the bulb of which is midway between the ends of the exposed mercury thread.

0.000154 = apparent coefficient of expansion mercury in glass.

$C$  = the correction in degrees.

Then  $C = N(T - i) + 0.000154$ .

**188. Spot test.** One or 2 c.c. of the oil are poured on a porcelain plate and a drop of concentrated sulphuric acid is added carefully. If pure, the spot formed will bear a marked resemblance to a begonia leaf. If rosin or rosin oil be present, a black gummy mass immediately results; cottonseed oil gives a spot without the characteristic markings of the linseed-oil spot. Mineral oils give a scum band, rapidly spreading out over the surface from the drop, the margin of the band being uniformly circular. Fish oils give a similar reaction, but the margin of the band is not at all uniform and may be readily distinguished from mineral oils. With a little practice and working with oils of known composition this test can be relied upon to detect any appreciable adulteration with the above oils.

**189. Mineral oils.** The spot test for petroleum products may be confirmed by allowing a sample of

the oil to flow down a sheet of glass the other side of which has been painted jet black. If petroleum products are present even in a minute quantity, the sample will exhibit the "bloom" characteristic of mineral oils. A standard sample should always be run for comparison. It is possible to remove the "bloom" of mineral oils by the use of nitrobenzene, nitronaphthalene, or similar compounds, but the author is of the belief that this is very seldom resorted to in paints, although it is frequently done in liquid polishes and floor compounds.

**190. Quantitative estimation of mineral oil.** Quantitatively the mineral oil may be estimated by saponifying 10 grams of the oil with alcoholic potash for 2 hours, using a return condenser. The alcohol is distilled off and the soap dissolved in 75 to 100 c.c. of water, transferred to a separatory funnel, and 50 c.c. of ether added. The liquids are then shaken, avoiding the formation of an emulsion as far as possible. The aqueous solution is then drawn off, the ethereal layer washed with a few cubic centimeters of water to which a little caustic potash has been added, and poured into a weighed flask. The soap solution is then returned to the separator, and twice extracted with ether in the same way as before.

The combined ethereal solutions are distilled off on the water bath, and the flask dried and weighed. The increase in weight represents the amount of unsaponifiable matter, and unless rosin oil is present, represents the mineral oil with the exception of about 2 per cent, the average amount of unsaponifiable matter in linseed oil.

**191. Separation of mineral oil from rosin oil.** The mineral oil may be separated from the rosin oil in the

unsaponifiable material by heating 50 c.c. of nitric acid of 1.2 specific gravity to boiling in a flask of 700 c.c. capacity, the source of heat removed, and the unsaponifiable material added. The flask is then heated on the water bath with frequent shaking for about one-half hour, and 400 c.c. of cold water added. After cooling, 50 c.c. of petroleum ether are added and the flask agitated, the mineral oil is dissolved, while the resinous matters remain in suspension. The liquid is then poured into a separatory funnel, leaving behind as much of the resinous material as possible. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a weighed flask. Another portion of petroleum ether is added to the rosin remaining in the flask, and allowed to act upon it for about ten minutes, when it is added to that in the weighed flask. After distilling off the ether the oil is weighed. Mineral oils lose about 10 per cent when treated with nitric acid in this way, and hence the weight of the oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

**192. The Outerbridge test for mineral oil and rosin oil.** A few drops of the oil to be tested are placed between two plates of clear glass, placed against a black background and examined by reflected light from an inclosed arc lamp, adjusted to show a faint rosy light in addition to the powerful white light. The presence of mineral oil is evidenced by a greenish fluorescence, of rosin oil by a bluish fluorescence. Even the so-called debloomed oils show up strongly under this test. By preparing a set of standards of known composition as to percentages of mineral or rosin oils, and judging the sample under examination by comparison, reducing it, if necessary, with a known

amount of pure vegetable oil until it corresponds in fluorescence with one of the standards, the approximate percentage of rosin or mineral oil may be determined. For this purpose 50-c.c. oil test bottles may be used. The value of the test depends on the enormously intensified fluorescence due to the particular source of light employed.

**193. Cottonseed oil.** This oil is seldom found in house paints, but is often used in the cheaper class of barn paints. The spot test may be confirmed by the Halphen test, the apparatus required being a large test tube with a condensing tube and a brine bath; the reagent employed being a 1.5 per cent solution of sulphur dissolved in carbon bisulphide with an equal volume of amyl alcohol added. Equal volumes of the oil and reagent are heated in a steam bath at first, and, after the violent boiling has ceased, in the brine bath at 105–110° C. for about 30 minutes. As little as 1 per cent of cottonseed oil will give a crimson wine coloration. Cottonseed oil heated to 250° C. does not respond to this test.

**194. Corn oil.** This oil gives a spot test much resembling that given by linseed oil, but may be detected in linseed oil, if in quantity, by the following test: Dilute with four volumes of benzine, add one volume of strong nitric acid, shake. Linseed oil turns a white color, while corn oil turns a reddish orange.

**195. Menhaden oil.** In addition to the spot test this oil may be detected by rubbing a little of the sample vigorously between the palms of the hands or by heating a few c.c. in a porcelain crucible. Fish-oil mixtures give the characteristic odor of oils of this class. In case of doubt the Eisenschyml test (see section 128, Chapter IX) may be used.



**196. Rosin and rosin oils.** These products are best detected qualitatively by means of the Liebermann-Storch reaction, which is of sufficient delicacy to detect the presence of even very small quantities of rosin oil or rosin drier in boiled oil. Shake 1 to 2 c.c. of the oil under examination in a test tube with acetic anhydride at a gentle heat, cool, pipette off the anhydride, and place a few drops on a porcelain crucible; cover, and add one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin or rosin oil is present a characteristic violet, fugitive color results. Certain fish oils will give a very similar color, but if present are easily detected by the fishlike odor of the oil on warming.

Old samples of pure boiled oil give a color that might be easily mistaken for rosin or rosin oils; in such cases it is best to warm the oil with alcohol so as to extract the bulk of rosin present and test the alcoholic extract. Rosin may be more completely separated and estimated by Twitchell's process (J. Soc. Chem. Ind., 1891, 10, 804) or by Gladding's method (Amer. Chem. J., 3, 416). This process depends upon the solubility of silver resinate in ether, while the silver salts of fatty acids are insoluble.

**197. Soya bean oil.** This oil has come into use quite largely during the last few years. Its chemical and physical properties are so nearly like those of linseed oil that it is difficult to detect it with certainty when mixed with linseed oil, unless more than 20 per cent is present, in which case the oil will be below the accepted limits as to iodine number and specific gravity.

A determination of the oxygen absorption value of the oil under examination frequently gives important



information as to its purity. The rate of absorption is much slower and the amount of oxygen absorbed is materially less in mixtures of linseed oil with soya, cottonseed or corn oils. For this purpose five very thin sheets of aluminum, 3 in. by 6 in., supported by a single framework of aluminum wire which separates the plates by three-eighths of an inch, are used. About two drops of oil are applied evenly over each sheet, the total weight of oil used being between 0.5 and 0.7 gram. The apparatus is suspended under a shelf to avoid dust particles and in a good light and is weighed daily. This particular type of apparatus has been used by a number of chemists, including the author, with very satisfactory results.

**198. Reducing oils and driers.** The percentage of volatile thinner obtained and the consistency of the nonvolatile vehicle, taking into consideration the character of the product, will indicate to some extent the amount of reducing oil present. Frequently excessive quantities of liquid driers are used and the nonvolatile portion of the drier will disguise to a large extent the character of the oil used. If it becomes necessary to determine the amount of gums or resins associated with the oil, the procedure given in Chapter XIX may be followed.

## CHAPTER XV

### EFFECT OF STORAGE ON THE COMPOSITION OF PAINTS

**199.** The changes undergone by certain types of paints on standing for various periods have been investigated by R. E. Christman, the holder of the Acme White Lead & Color Works, 1916, Research Fellowship at the University of Michigan, and are presented in brief form herewith. These or similar reactions occur to a much less degree in many varieties and classes of paint products and, unless clearly understood, may easily mislead the analyst, whose purpose in making the analysis is to correct or explain the trouble.

**200. Need for emulsifiers.** One of the earliest difficulties encountered in the manufacture and use of paints was the tendency of the heavy pigments to settle from the vehicle if the paint were permitted to stand for a considerable time before use. It was soon discovered, however, that the addition of a small amount of water containing a suitable emulsifying agent helped to prevent this settling of the pigment. But while eliminating one source of difficulty, this practice has brought on other troubles.

**201. Effect of Emulsifiers.** Some emulsified paints, if allowed to stand in storage for a year or more, will show evidence of deterioration which manifests itself in one of two ways, either through the formation of

an amorphous soapy blanket between the settled pigment and the supernatant vehicle or by the gelatination of the entire paint to a mass of about the consistency of soft putty, the vehicle seemingly having disappeared entirely. The first case is usually spoken of as "skinning" and the second as "puttying" or "livering."

Christman found that this blanket, in white lead and zinc oxide paints with a small percentage of water, contained 13 to 16 per cent of lead and zinc oxides, in the ratio of 7 parts of zinc oxide to 1 part of lead oxide, indicating that zinc oxide was the active agent. The oil extracted from the pigment had an apparent free acid value of 15 to 16.

**202. Hydrolysis of lead and zinc soaps.** Since these salts of linseed oil are easily hydrolyzed, it is apparent that their presence in the dissolved state would cause an oil to show an acid value which would include the amount of alkali necessary to hydrolyze the soaps as well as that required to neutralize the free fatty acids. It is well known that the limits of the acid number on a boiled oil are higher than those on a raw oil, and the difference is evidently due to the amount of metallic soap present as well as the increase in the true acid content. The same difficulty would be experienced in attempting to follow the progress of the hardening of rosin by zinc or lime. The operator may try to determine the extent of the neutralization by titration with alkali, but it is evident that his results will show an acid content far above what is actually present.

Christman presents the results obtained with mixtures of water and linseed oil and various emulsifying agents and pigments, for various intervals of time.

TABLE XXII

**203. Effect of emulsifying agents**

No.	Emulsifying agent	Time	Acid Number
1.	Linseed oil used.....	..	2.98
2.	Linseed oil & water.....	2 h.	3.95
3.	Sodium carbonate.....	2 h.	5.93
4.	“ “.....	18 h.	22.28
5.	“ “.....	22 h.	34.10
6.	Casein.....	18 h.	5.58
7.	Chloride of lime.....	24 h.	151.70
8.	Borax.....	24 h.	9.55
9.	Zinc oxide.....	18 h.	7.38
10.	White lead.....	20 h.	7.60

These results show that water itself has a small action upon linseed oil, the action being increased through the emulsion. Of the more common emulsifying agents, borax has the least effect, the carbonate exerts a marked action, while the chloride of lime is the most powerful of all. The so-called active pigments are almost without action.

**204. Reaction in paint on storage.** When ready-mixed paints are stored, the first general reaction is this hydrolysis of the oil by the water hastened by the presence of the alkali. The pigment itself may have some effect upon the rate, but its chemical action is undoubtedly very small. The hydrolysis is necessarily slow since the oil and water are immiscible and since some of the carbonate is removed by the zinc oxide. Before any large amount of acid is formed, the pigment has settled to a great extent, leaving the clear vehicle above. The acid and oil have their own kinetic motions and the acid, coming in contact with the top of the settled pigment, reacts with the basic pigments. The zinc oxide is the most basic and the most active and combines with the acid with the formation of the zinc soap.

**205. Insolubility.** The zinc soap formed on the neutralization of the acid is almost completely insoluble in the cold vehicle and is at once precipitated out on top of the pigment. The white lead also unites with the acid with the formation of the lead soap and is carried down with the zinc, which builds up and forms the peculiar skin over the pigment. This reaction between the acid and the pigment takes places readily, so that the oil never shows a pronounced free acid value. This value was determined as 15-16, and when allowance is made for the difference due to the soaps dissolved, it is lowered to about eight.

**206. Puttied paint.** This designation is usually applied to paints in which the liquid vehicle has apparently disappeared, the entire mass being of a solid or semisolid consistency. The analysis of such paints will usually reveal a considerable percentage of water and of rosin added either as gloss oil or as a short oil tung oil-rosin combination. The reactions occurring in such paints may be summarized in the following manner. Although the rosin in the gloss oil is usually limed, there still remains a high content of the free rosin acid. This acid is very active and its combination with basic pigments takes place in a very short time.

The metallic rosinates formed are soluble in the vehicle but cause it to become more viscous and the pigment is held up much more readily throughout the entire paint. On standing, the water carries on its destructive action on the oil, and since the amount of water and alkali are usually larger in this class of paints, the action is consequently faster. The acid of the oil is slowly liberated and comes in contact with pigment still remaining distributed throughout the



vehicle portion. The metallic salts, especially the zinc, are formed, but due to the high viscosity of the vehicle are unable to drop out and remain suspended in the oil. Since the rosin acid has such great activity, there is very little free rosin acid remaining, for this would be entirely neutralized before the oil soaps really begin to form. The vehicle portion becomes constantly thicker and the pigment and metallic oil soaps are held up in a very finely divided condition.

**207. Colloidal formation.** The rosinate in the oil is probably more in a colloidal state than in a true solution and as the oil content decreases, due to the lesser solubility of the rosinate in the volatile thinner, it tends to drop out in the solid form. When the content of the precipitated metallic salts becomes high enough, we have a condition where the vehicle is more in solution in the solid constituents than in suspension in the liquid, and the resulting state is what is termed "puttied."

Since, during the progress of the reaction, the acids and pigment are in intimate contact, the opportunities for reaction are much better and the oil acids are neutralized almost as fast as liberated, accounting for the corrected low free acid content of the extracted oil. As in the settled pigment of the skinned paint, the tendency is again to the formation of the basic soaps. But if the rosin in the gloss oil is highly limed or for any similar reason the pigment should settle before the oil acids become sufficiently large in amount, the action would be one of skinning rather than livering.

TABLE XXIII

208. Effect of storage on drying oils, extending over a period of eight years<sup>1</sup>

	Specific Gravity	Iodine Number	Saponification Value	Acid Value
Raw Linseed Oil				
March, 1911 .....	.931	186	188	2.0
Nov. 1914 .....	.933	185.4	189.6	2.8
Sept. 1916 .....	.936	176.9	190.2	3.3
Feb. 1919 .....	.943	182.1	192.3	4.8
Perilla Oil				
March, 1911 .....	.940	180	188	2.0
Nov. 1914 .....	.940	172	195.4	7.4
Sept. 1916 .....	.939	....	193.3	14.8
Feb. 1919 .....	.941	168.9	192.1	10.5
Tung Oil				
March, 1911 .....	.944	166	183	3.8
Nov. 1914 .....	.946	161.5	190.3	5.7
Sept. 1916 .....	.944	158.6	188.7	5.6
Feb. 1919 .....	.948	141.1	191.6	6.0
Soya Oil				
March, 1911 .....	.924	129	189	2.3
Nov. 1914 .....	.925	130.2	193.1	4.7
Sept. 1916 .....	.937	122.0	192.1	7.0
Feb. 1919 .....	.939	121.7	193.4	7.8

TABLE XXIV

209. Effect of storage on linseed oil with various pigments after two years<sup>2</sup>

Pigments	Specific Gravity	Iodine Number	Ash Per Cent
Original oil .....	.934	179.6	0.13
White lead (carbonate) .....	.938	177.3	0.40
Zinc oxide .....	.934	179.7	0.13
Chrome yellow .....	.935	175.7	0.14
Indian red .....	.939	172.5	0.14
China clay .....	.936	171.6	0.14
Flake graphite .....	.933	178.2	0.15
Artificial graphite .....	.939	180.8	0.15

<sup>1</sup> Paint Researches, Gardner, p. 304. Circular No. 60, Paint Mfrs. Association.

<sup>2</sup> Boughton, J. Ind. & Eng. Chem., 5, 282.

**210. Iodine number.** In order for the iodine number to furnish reliable information regarding the nature of the oil used in a paint which has been prepared or in storage for some length of time, it is necessary to saponify the extracted vehicle, separate the fatty acids and determine their iodine value, instead of determining the iodine value of the oil. As the iodine value of the fatty acid is about 4 per cent greater than that of the glyceride, the minimum limit according to Boughton for oil from North American seed should be about 185 and from South American seed 178. Due precautions should be observed to prevent oxidation during the preparation of the fatty acids, as described in Chapter X, Separation of Vehicle from the Pigment.

## CHAPTER XVI

### ANALYSIS OF SOLID AND LIQUID DRIERS

**211. Materials used.** The paint or varnish manufacturer usually prepares his own driers by combining the metallic salts or oxides with linseed oil, rosin, hard gum resins, or tung oil, or combinations of these products, giving linoleates, resinates, or tungates as the case may be. The combinations may be effected in either of two ways, by fusion or direct heat, and by precipitation of the soaps from the solutions of the corresponding salts.

The metallic salts or oxides commonly used in the preparation of driers are:

Litharge  
Red lead  
Acetate of lead  
Oxide of manganese  
Borate of manganese  
Zinc sulphate  
Zinc oxide  
Cobalt acetate

The majority of drier manufacturers purchase their resinate of manganese and resinate of cobalt instead of attempting to effect the combination themselves. Many baking blacks also contain American (Prussian) blue and various iron soaps which serve to increase the toughness and degree of blackness.

**212. Lead compounds.** The examination of lith-

arge and lead acetate offer no difficulties. Red lead always contains unconverted litharge and it is therefore advisable to determine the true red lead content. The author does not agree with many drier manufacturers that red lead should be valued according to the percentage of true red present in it. Certain physical characteristics are even more desirable than a high red lead content. A low gravity red lead (14 g. to 18 g.), of a high percentage of conversion, is much more difficult to combine with oil because of its tendency to "ball" than a coarse red lead (35 g. to 40 g.) having a red lead content of 60 per cent to 80 per cent, providing it is made from a soft massicot at a moderate temperature, and the drying qualities of the resulting product are fully as satisfactory as if a high conversion red lead were used.

### 213. Determination of true red lead content.<sup>1</sup>

Weigh 1 g. of finely ground sample into a 200-c.c. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 g. of c.p. "Tested Purity" crystallized sodium acetate, 2.4 g. of c.p. KI, 10 c.c. of water and 10 c.c. 50 per cent acetic acid; stir until all is liquid, warming gently; if necessary add 2 to 3 c.c. of water, cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 c.c. of water containing 5 or 6 g. of sodium acetate, and titrate at once with decinormal sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undis-

<sup>1</sup> Am. Soc. for Test. Mat. Stds., 1918, p. 651



solved particles up with the rod until free iodine no longer forms, wash off rod, add the sodium-thiosulphate solution until *pale yellow*, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of sodium thiosulphate that had been added.

**214. Calculation.** The iodine value of the sodium-thiosulphate solution multiplied by 0.94193 =  $\text{PbO}_2$ ; the iodine value multiplied by 2.69973 =  $\text{Pb}_3\text{O}_4$ ; the  $\text{PbO}_2$  value multiplied by 2.86616 =  $\text{Pb}_3\text{O}_4$ .

The sodium-thiosulphate solution and the starch solution shall be prepared as follows:

**215. Sodium-thiosulphate solution (decinormal).** Dissolve 24.83 g. of c.p. sodium thiosulphate, freshly pulverized and dried between filter paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made. The solution is best made with well-boiled water free from  $\text{CO}_2$ , or let stand 8 to 14 days before standardizing. Standardize with pure, resublimed iodine, as described in Treadwell-Hall, "Analytical Chemistry," Vol. II, p. 602 (1910), and also against pure potassium iodate; the two methods of standardization should agree within 0.1 per cent on iodine value.

**216. Starch solution.** Stir up 2 to 3 g. of potato starch with 100 c.c. of 1 per cent salicylic-acid solution, and boil the mixture till starch is practically dissolved, then dilute to 1 liter, or as per Lord.<sup>1</sup>

If sample contains an appreciable amount of nitrite (nitrate has no effect on method), leach out water-soluble matter, dry residue and determine  $\text{PbO}_2$  as above, calculating to basis of original sample.

**217. Oxide of manganese.** The fineness of the

<sup>1</sup> Notes on Metallurgical Analysis, page 103 (1903).

particles is an important factor in determining the suitability of this product for use in driers and varnishes. Numerous practical tests made by the author show that there is only a slight difference between particles that pass a 200-mesh screen and those that pass a 300-mesh screen, in the total percentage of manganese that will combine with the oil during a normal cook. The residue that remains on a 200-mesh screen, however, enters into combination much more slowly and incompletely and this residue should be kept to as low a percentage as possible.

**218. Procedure.** The manganese content is best determined by the ferrous sulphate method.<sup>1</sup>

*Ferrous sulphate solution.* Carefully dissolve 90 g. ferrous sulphate in 200 c.c. sulphuric acid (1.84) and 900 c.c. distilled water. Standardize against the potassium permanganate solution each time before using.

*Potassium permanganate solution.* Dissolve 10 g. potassium permanganate solution in distilled water and make up to 1000 c.c., allow to stand overnight or preferably several days. Standardize against ferrous ammonium sulphate or sodium oxalate.

**219. Determination.** Weigh 0.5 g. into a 250-c.c. Erlenmeyer flask, add 50 c.c. standard ferrous sulphate solution, cover with watch glass and heat to boiling until solution of the manganese is effected. Dilute to about 150 c.c. and titrate with the standard permanganate solution in the usual manner.

**220. Resinate of manganese.** The percentage of manganese in this product varies greatly. In the precipitated variety the best grades will contain approximately 7 per cent manganese. The fused variety runs much lower owing to the fact that when

<sup>1</sup> Barneby, J. Ind. and Eng. Chem. 9, 961 (1917).

the maximum amount of manganese is used, the product will contain considerable insoluble material and be very black in color. It should, however, contain not less than 1.75 per cent manganese.

**221. Procedure.** The manganese content can be determined by incinerating a weighed quantity of the resinate in a large crucible. Extract with boiling water to remove soluble salts, decant through a filter paper, then incinerate the paper in the same crucible. Moisten the ash with a few drops of nitric acid to oxidize any reduced oxide, heat to expel the acid, dissolve with a measured quantity of the standard ferrous sulphate solution and titrate with permanganate as described under Oxide of Manganese.

**222. Borate of manganese.** The composition of manganese borate is more or less a matter of dispute, because of the fact that when the precipitated borate is washed, it continually loses boric acid. It can therefore be washed in the press to a very slight extent only as the dried product otherwise turns brown, owing to the separation of manganese oxides. The best commercial grades have a manganese content of about 18 per cent. The author has examined samples containing as low as 10 per cent. As the value of manganese borate in a varnish is due essentially to the manganese content, it is advisable that an accurate method of analysis should be selected.

**223. Procedure.** Heckel<sup>1</sup> made an extended investigation of the methods in use, including the bis-muthate, Ford, and Ford Williams methods. With certain essential modifications, he found the last to be the most accurate and suitable for the examination of manganese borates. The author has found this

<sup>1</sup> Drugs, Oils and Paints, Aug. 1918, page 80.

method with additional cautions very satisfactory, not only for manganese borates but with complex drier mixtures. This determination is made as described beginning with section 230. A 1-gram sample is used and dissolved in the one-third nitric acid.

**224. Cobalt resinate.** The variety commonly used is the fused, the best grades of which contain about 2 per cent of cobalt. The preferable method of analysis is to dissolve the ash in hydrochloric acid, precipitate with nitrite of potash, filter, wash thoroughly, dissolve in sulphuric acid and evaporate until fumes appear, then make alkaline with ammonia and deposit the cobalt by electrolysis. If the necessary apparatus is not available the following method will give satisfactory results.

**225. Procedure.** Incinerate a weighed quantity of the resinate, igniting the ash thoroughly, cool and weigh. Dissolve in hydrochloric acid, adding a small quantity of water and filter. Add 5 c.c. sulphuric acid to filtrate and evaporate to dryness in a porcelain evaporating dish and weigh as sulphate, the sulphate being stable at moderate temperatures. If desired, the sulphuric acid solution after running down to fumes to remove the hydrochloric acid may be neutralized with ammonia and the cobalt precipitated as  $\text{CoNH}_4\text{PO}_4$  as described in section 241.

**226. Determination of the metallic driers that may be present in varnishes, liquid driers, and vehicle mixtures.** Due to the fact that paint or enamel vehicles, driers and varnishes are frequently blends of two or more very different products, it is not unusual for the analyst to be confronted with a mixture containing lead, copper, or iron as impurities from the varnish kettle, or iron from iron linoleates or other soaps,



manganese, cobalt, and calcium, and occasionally zinc, e.g., a mixing varnish containing lead and manganese may be mixed with another varnish containing cobalt and limed rosin (calcium rosinate) in order to meet certain requisites as to color, toughness, gloss, body working qualities and service value.

The prevailing practice of incinerating the drier and determining the lead and manganese in the ash will give results that are too low on the lead content, as from 5 to 15 per cent of the lead is lost when burning at a low red heat.

The following procedure avoids any loss from the volatilization of the lead, and under favorable conditions the decomposition can be completed in 3 hours and is equally suitable for lead and manganese only, or for complex mixtures.

**227. Analytical procedure.** In order to secure sufficient quantities of the metallic compounds to render the analytical procedure reasonably accurate, it is advisable to take two samples of approximately 20 grams each, which are weighed into 600-c.c. beakers, the volatile thinners driven off as rapidly as possible, 100 c.c. concentrated sulphuric acid added and heated gently at first to avoid excessive frothing, then heated vigorously with frequent stirring until almost all of the gum and oil have been oxidized with reduction of the acid to sulphur dioxide. The black solution is allowed to cool somewhat and 65 per cent perchloric acid added in small portions, 5 c.c. to 20 c.c. in all. After heating about 30 minutes longer, the solution should entirely clear up and is then evaporated to a bulk of 3 c.c. to 5 c.c., diluted with water and the lead sulphate filtered off on to a porcelain Gooch crucible, carefully reserving the filtrate.



In most cases, if the sulphuric solution is evaporated to dryness, the residue chars and to remove every trace of organic matter, it must again be boiled with sulphuric acid and 25 c.c. potassium or ammonium perchlorate added and again evaporated to remove most of the sulphuric acid. Sometimes it may be necessary to evaporate practically to fusion of the bisulphate formed. This last trace of organic matter does not seem to interfere in any way with the determination of the lead, the only requisite being that the brown color of the solution due to organic matter shall completely disappear.

**228. Lead.** The lead sulphate is redissolved in a suitable quantity of ammonium acetate solution, filtered, neutralized with ammonia and made *just barely acid* to litmus with dilute hydrochloric acid (1 to 10), dilute to about 350 c.c. A comparatively small quantity of free acid will prevent some of the lead from precipitating. Precipitate the lead with hydrogen sulphide. Settle, filter, and wash with cold water.

If calcium is to be estimated, 10 c.c. to 15 c.c. of sulphuric acid are added to the filtrate from the lead sulphide in an evaporating dish, heated over a fairly hot flame until all of the acetic acid and almost all of the ammonium sulphate have been driven off. Cool, redissolve in sufficient water and add to the filtrate from the copper sulphide, section 229.

Place filter and lead sulphide precipitate in 25 c.c. of nitric acid and 25 c.c. of water, heat gently until the lead has all dissolved, as shown by the residual sulphur having a yellow to whitish color. Do not boil hard enough thoroughly to disintegrate the filter paper. If difficulty is experienced in dissolving the

lead contained in the sulphur particles, it is better to collect them into a ball with the aid of a stirring rod and remove to a small beaker and treat with a few cubic centimeters of concentrated nitric acid, and heat until dissolved, then pour back into the larger beaker.

Pour solution and filter paper on to a suction funnel provided with a platinum cone. If any fine particles pass through, pour the filtrate back again. This procedure permits the washing of the filter mass with a very small amount of water, thus saving considerable time in the subsequent evaporation. Add 5 c.c. of dilute sulphuric acid to filtrate, and evaporate until sulphur trioxide fumes appear. Cool, add 25 c.c. of water, 25 c.c. of alcohol; allow to stand one-half hour with occasional stirring; filter, using Gooch crucible, wash with dilute alcohol, dry, heat gently over ordinary lamp, and weigh as lead sulphate.

**229. Copper.** If a highly acid gum has been used, appreciable traces of copper will be found present and constitute an impurity which need not be estimated but must be removed.

The filtrate from the original lead sulphate (section 227) is treated with hydrogen sulphide and filtered to remove any copper sulphide formed. The concentration of sulphuric acid should be about 5 per cent during the precipitation. This filtrate is combined with the filtrate from the lead sulphide (section 228), which may contain a portion of the calcium, and the combined filtrate boiled until all traces of hydrogen sulphide have disappeared, the removal of which can be assisted with the addition of a few drops of bromine water.

**230. Manganese.** The above solution is evaporated nearly to dryness in a porcelain evaporating dish.

Dissolve in 30–40 c.c.  $\frac{1}{3}$  colorless nitric acid, allowing sufficient time for any calcium to go into solution. If a large quantity of calcium is present, the amount of dilute nitric acid must be increased accordingly. Filter off the insoluble if any. Pour into a 250-c.c. graduated flask and make up to the mark with distilled water. Shake until the contents of the flask are thoroughly mixed and pipette out a 100-c.c. aliquot portion.

**231. Precipitation of manganese.** Place this aliquot in a 400-c.c. beaker, add 50 c.c. of 1–1 *colorless* nitric acid; heat to boiling, then add cautiously three grams of solid sodium or potassium chlorate. The solution is now boiled for fifteen minutes or until it is thought that all of the manganese has been precipitated as manganese dioxide. Three grams more of sodium or potassium chlorate and 15 c.c. more 1–1 nitric acid are added to the solution, and then the solution is boiled down to a total volume of about one-third or one-fourth of the original volume in order to make certain that all of the manganese has been precipitated. Sodium chlorate is preferable to the potassium salt as it is easier to wash out. A colorless nitric acid must be used, otherwise some of the manganese dioxide is reduced and dissolved.

If a purple color forms here, it is an indication that some permanganic acid is being formed and the solution should be boiled until this color disappears.

**232. Filtration of precipitate.** A filter meanwhile has been prepared by placing in the neck of an ordinary 60° long-stemmed funnel, enough glass wool to fill the funnel proper about one-third full. The glass wool is tucked in the funnel tightly with the finger and then covered with a good dense layer of asbestos

fiber, the asbestos being placed on the glass wool by pouring through the funnel a thick emulsion of finely divided asbestos fiber.

The manganese precipitate in the beaker is allowed to stand for a few minutes until fairly cool, and is then filtered through the glass wool and asbestos. Great care must be exercised in order to prevent a suspension of finely divided manganese precipitate from creeping over the top of the asbestos and glass wool filter and running through into the filtrate.

**233. Washing.** One other difficulty which must be guarded against is the tendency of the manganese dioxide to run through in a colloidal state. This tendency is increased by washing the precipitate with boiling water, and it should therefore be washed carefully with small portions of warm, not hot, water. If the precipitate runs through in a colloidal form, the manganese may be reprecipitated by placing the filtrate containing the manganese on the hot plate, adding a large excess (4-5 grams) of additional potassium or sodium chlorate and 20-30 c.c. 1-1 nitric acid and boiling until the colloid coagulates and the manganese is reprecipitated.

The precipitate in the funnel is next washed with hot water containing a little nitric acid and finally with hot distilled water until the filtrate is *free* from acid. As stated above, care and judgment must be used in washing the precipitate on the filter, because too much washing, especially with boiling water, seems to produce a tendency for the precipitate to become colloidal and run through.

**234. Solution of precipitate.** The precipitate together with the glass wool asbestos mass is next removed from the funnel and replaced in the beaker



in which the original precipitation was made; a solution of ferrous sulphate of known strength is run down the sides of the funnel to remove the last traces of manganese dioxide, the funnel during this operation draining into the beaker containing the precipitate. The funnel is washed out with distilled water and an excess of standard ferrous sulphate solution is then run on to the precipitate in the beaker from the same burette used in washing down the funnel.

The asbestos mass is stirred and agitated with a number of small pieces of small-diameter glass rods during the addition of the ferrous sulphate solution. If difficulty is experienced in entirely dissolving the manganese precipitate, it must be manipulated with a glass rod until the glass wool-asbestos mass is practically white in color and shows no black particles in it.

**235. Titration.** The solution of the precipitate in the excess of ferrous sulphate is then titrated with a solution of potassium permanganate, until a pink color is produced not disappearing under 2 or 3 minutes. Read the burette and deduct the amount used from that to which the amount of ferrous sulphate taken would have been equivalent; the difference is equivalent to the Mn present in the precipitate. This, corrected by the factor for the permanganate solution, will give the amount of Mn in milligrams.

The preparation of the standard solutions, the reactions involved and the calculations required are very clearly stated in the following excerpt from Lord and Demorest's Metallurgical Analysis under the Ford-Williams method.

**236. Preparation of the permanganate solution.** Dissolve 1.151 grams of pure  $\text{KMnO}_4$  in water and dilute to 1 liter. One cubic centimeter of this solu-



tion will have the same oxidizing power as 0.001 gram of manganese in the form of the brown precipitate ( $\text{MnO}_2$ ). Check the solution against pure iron or pure ammonium ferrous sulphate  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Dissolve 0.1425 gram of the salt in 50 c.c. of water containing 2 c.c. of  $\text{H}_2\text{SO}_4$ . This should consume just 10 c.c. of the permanganate solution. Run in the solution until the last drop gives a permanent pink color.

If more or less than 10 c.c. is required, calculate the amount of Mn to which each cubic centimeter of the permanganate is equivalent by the proportion,  $0.001 : x = n : 10$ ,  $n$  being the number of cubic centimeters of solution used in the test, and  $x$  the required value.

**237. Preparation of the ferrous sulphate solution.** Dissolve 20.18 grams of pure crystallized ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) in about 500 c.c. of water, to which 25 c.c. of concentrated  $\text{H}_2\text{SO}_4$  have been added, and then dilute to 1 liter.

Determine its strength against the permanganate solution by measuring 15 c.c. with a pipette into a beaker, adding about 25 c.c. of water and 1 c.c. of  $\text{H}_2\text{SO}_4$  and then running in the permanganate till the pink color is permanent. About 30 c.c. should be required. This value must be determined frequently, as the solution of ferrous sulphate alters rapidly from the oxidizing action of the air. In large amounts it is best kept in a carboy and covered with a layer of kerosene oil to keep out air. The solution can be preserved in this way for some time with but little alteration, and can be drawn out by a siphon as needed.

**238. Calculations.** From the two formulas already given we have the relations between the  $\text{MnO}_2$ ,  $\text{FeSO}_4$  and  $\text{KMnO}_4$  as follows:

One atom of Mn in the form of brown precipitate ( $\text{MnO}_4$ ) will oxidize two atoms of Fe as ferrous sulphate. Two molecules of permanganate will oxidize ten atoms of Fe as ferrous sulphate, that is to say, two molecules of permanganate will oxidize the same amount of iron as will five molecules of  $\text{MnO}_2$  containing five atoms of manganese. Therefore, to find how much  $\text{KMnO}_4$  will be needed to have the same oxidizing power as 0.001 gram of Mn in the form of the brown precipitate we have the proportion:

5 atoms Mn: 2 mol.  $\text{KMnO}_4$  = 275: 316.3 = 0.001:  $x$ , which gives  $x$  = 0.00115 gram, the amount of  $\text{KMnO}_4$  to be dissolved in 1 c.c. if 1 c.c. is to be equivalent to 0.001 gram Mn as "brown precipitate." This is 1.151 grams in a liter.

To determine the amount of iron or of ammonium ferrous sulphate to which 1 c.c. is equivalent, we have:

1 atom Mn: 2 atoms Fe = 55: 112 = 0.001:  $x$ , in which  $x$  is the required amount of iron. The value of  $x$  is 0.002034. To determine the amount of the ammonium ferrous sulphate, as this contains one-seventh of its weight of iron, multiply the value of  $x$  by 7 = 0.01425 for 1 c.c., or the figure given in the directions for 10 c.c.

That 15 c.c. of the ferrous sulfate solution may be equivalent to 30 c.c. of the permanganate it must contain 0.06102 Fe. This corresponds to 20.18 grams of  $\text{FeSO}_4, 7\text{H}_2\text{O}$  to the liter.

The filtrate from the manganese precipitate should be reserved for estimation of iron, if present, and cobalt.

**239. Iron.** In black baking Japans, iron linoleate or other iron soaps are generally present in considerable quantity. Driers cooked in an iron kettle usually

contain appreciable traces of iron and it is therefore advisable to recognize the possibility of its presence and provide for its elimination and, if desired, its estimation.

To the filtrate from the oxide of manganese precipitate are added 5 grams ammonium chloride, and the solution is made barely alkaline with ammonia and filtered boiling hot. If a considerable precipitate of ferric hydroxide is obtained it may contain a small amount of the cobalt and calcium. It should therefore be redissolved in hydrochloric acid, again precipitated with ammonia and the filtrate added to the first filtrate from the ferric hydroxide.

If the percentage of iron is desired, the ferric hydroxide precipitate is dissolved in hydrochloric acid, sulphuric acid added, run down to fumes, diluted with water, reduced with an aluminum spiral or metallic zinc and titrated with permanganate in the usual manner.

**240. Cobalt.** The filtrate from the ferric hydroxide precipitation will contain any cobalt present, calcium from the limed rosin and occasionally zinc, which is sometimes used for hardening rosin instead of lime. If zinc is suspected of being present it may be separated by the Zimmerman<sup>1</sup> method. Otherwise the filtrate from the ferric hydroxide is made distinctly alkaline with ammonia and treated with hydrogen sulphide, the black cobaltous sulphide filtered off and the filtrate reserved for the estimation of calcium if desired.

**241. Precipitation.** The cobaltous sulphide is dissolved in nitric acid, 5 c.c. sulphuric acid added run down to fumes to remove all traces of hydrochloric

<sup>1</sup> Treadwell & Hall, Analytical Chemistry, p. 158, 4th ed.

acid. Cool, add 25 c.c. water and ammonium hydroxide until only very faintly acid, otherwise all of the cobalt will not precipitate. In other words, the solution should be practically neutral. Add 10 times the weight (estimated) of the cobalt, of dry hydrogen ammonium phosphate, heat to almost boiling and hold at that temperature for 10 minutes. Cool, filter on to a weighed porcelain Gooch crucible, washing with a hot 1 per cent solution of hydrogen ammonium phosphate and finally with dilute alcohol. Dry at  $100^{\circ}\text{C.}$  to  $105^{\circ}\text{C.}$  and weigh as  $\text{CoNH}_4\text{PO}_4$ .

**242. Calcium.** The filtrate from the cobaltous sulphide is boiled thoroughly and the calcium precipitated in the usual manner with ammonium oxalate and estimated gravimetrically or volumetrically as desired.

## CHAPTER XVII

### COMPARATIVE ANALYSIS OF BLACK BAKING JAPANS

**243.** The author will not attempt to formulate an analytical procedure for the examination of air drying Japans and the various bituminous coatings for damp proofing stone, masonry, and concrete surfaces, as the ingredients that may be present are almost numberless and are difficult to identify when present in complex mixtures, as is frequently the case.

**244. Method.** The author does not believe that it is feasible to develop a purely analytical procedure that will differentiate the various constituents, together with the percentages thereof, of a baking Japan. However, if the analyst is familiar with the raw materials used, he can develop a method partly analytical and partly constructive that will enable him to arrive at an equivalent composition within very definite limits. A procedure suited to the requirements of one chemist may fail with another, or it may fail due to the presence of a new or unusual component. The working basis of the method herewith given as applied to baking Japans illustrates how the problem may be attacked and the manner of procedure developed as the analyst proceeds.

**245. Separation of the volatile portion.** Kerosene is usually present, therefore distillation by direct heat or with superheated steam introduces a serious error, as the temperature required to remove the heavy volatile fractions is sufficiently high to cause an appreciable amount of the asphaltum hydrocarbons and of



the fatty acid compounds of the stearine pitches to pass over with the petroleum thinners.

Distillation by boiling with water at 100° C. will not remove all of the volatile thinner without special precautions being adopted, as the viscous, gummy nature of the nonvolatile retains within itself the last portion of the thinner. To overcome this difficulty the following scheme may be adopted.

**246. Procedure.** A weighed amount (100 grams to 130 grams) of the Japan, together with 400 c.c. water, are placed in a 1-quart varnish can. A distilling bulb and overflow burette are used as described in Chapter XIII. The distillation is continued as long as any appreciable quantity of volatile thinner is obtained, the aqueous distillate being returned to the distilling can as needed.

TABLE XXV

Amount taken, 126 grams

## TYPICAL DISTILLATION OF VOLATILE THINNER

No. of Fraction	Aqueous distillate c.c.	Volatile thinner c.c.
1.....	250	90.2
2.....	200	4.1
3.....	200	2.1
4.....	200	1.6
5.....	200	1.5
6.....	200	1.1
7.....	200	0.8
8.....	200	0.6
9.....	200	0.6
10.....	200	0.4
11.....	200	0.2
Total.....	2250 c.c.	103.2 c.c.

**247. Solution.** The surplus water is removed from the distilling can, the last traces being driven off by a gentle heat, and the residue put into solution under a reflux condenser with 100 c.c. of pentane (Standard Oil Co.), using the fraction distilling between 50° C. to 60° C., and reserving the remaining portion from

which the 100-c.c. fraction is obtained, for subsequent addition. The pentane used should be a redistilled product, fractions above 60° C. being eliminated. A specially redistilled petroleum spirits can be used if the pentane is not available.

**248. Precipitation.** After solution, remove the contents of the can to an 800-c.c. beaker, add with constant stirring sufficient pentane, including the amount used and the portion reserved, to make a total of 600 c.c. pentane used. For complete removal from the can, it is advisable to cut the can open and wash out with a brush. Allow to stand 1 hour at 10° to 15° C. The bulk of the asphaltum and other gums present will be precipitated, leaving all of the oil in solution except a small percentage which is in combination with the lead and manganese. The precipitated gums are given two washings of 50 c.c. each of cold pentane, removed to a filter, dried and weighed. The precipitated gums are designated as the "break" and are discussed subsequently under the heading of Estimation of Gums.

**249. Distillation.** The pentane is distilled off from the liquid portion at a gentle heat on the electric hot plate, 400 c.c. of water added and the distillation continued as previously described, to remove the last of the heavy naphtha and kerosene. This volatile thinner is added to that obtained in the first distillation.

EXAMPLE: 126 grams taken, treated as previously described.

No. of Fraction	Aqueous distillate	Volatile thinner
	c.c.	c.c.
12.....	200	0.8
13.....	200	0.6
14.....	200	0.4
15.....	200	0.2
16.....	200	0.1
Combined totals.....	3250 c.c.	105.3 c.c.

The water is completely removed from the oil and soluble gum residue, due precautions being observed to prevent oxidation as described in Chapter XIX. This residue is weighed and treated as described under Estimation of Oil.

**250. Analysis of the volatile portion.** After determining the gravity of the volatile thinner it should be distilled in an Engler flask, electrically heated as described in Chapter II, and the distillation figures and solvent strength compared with those of the different petroleum thinners available. From this comparison a mixture can be calculated which will approximate the distillation desired. This is checked by a trial distillation and further revision made as may be found necessary, as the working qualities of a Japan depend very materially on the rate of evaporation and solvent strength of the thinners used.

**251. Sulphonation test.** Frequently coal tar naphthas or oils may be present, especially if the Japan in question is a very dense black, indicative of the presence of bone pitch, which is difficultly soluble when in considerable percentage with a straight petroleum thinner. This test is conducted on the recovered volatile thinner as described in Chapter XIII. It should be remembered that the natural asphaltic constituents of petroleum thinner react in the same way with aromatic hydrocarbons, as shown in the following table:

TABLE XXVI  
TYPICAL SULPHONATION TESTS

Product	Percentage of Reacting Hydrocarbons
P. & V. M. naphtha .....	8.0 per cent
Mineral spirits .....	12.5 " "
Heavy mineral spirits .....	12.0 " "
Kerosene.....	15.0 " "
Min. spts. 90% coal tar naphtha 10%.....	22.5 " "
Volatile thinners from Japan.....	14.5 " "

From the above table it is apparent that the recovered volatile thinner in question is free from coal tar naphthas or other volatile coal tar products.

**252. Estimation of gums.** The author has not found a method which will precipitate all of the gums that presumably may be present, without precipitating a portion of the heat-treated oils, and as an alternative has adopted the scheme previously described of precipitating as much of the gum as can be safely accomplished, without precipitating the oil.

The classes of gums, so called, that may be present are:

1. Asphaltums, of which gilsonite is most widely used.

2. Bone pitches, used especially because of their intense blackness.

3. Stearine pitches of varying degrees of consistency and blackness.

4. Petroleum pitches, varying in consistency from solid to semi-liquid. They are used chiefly in low-priced blacks, acid-resisting products, etc., and are not suitable for use in the medium and higher priced blacks such as usually reach the analyst, unless they have received special treatment, of which blowing with air under heat is the most common.

5. Varnish gums. The various resins used in the manufacture of the transparent varnishes are sometimes used in baking Japans to increase the gloss. Such use, however, is not generally looked upon with favor because of their tendency to make the coating brittle.

**253. Characteristics.** The various asphaltums, stearine pitches, and bone pitches to be found on the market differ greatly in their characteristics, but those

which can be used successfully in baking Japans fall within certain well-defined limits which eliminate a large number of these products as probable constituents. They must respond readily to treatment in the varnish kettle, must be freely soluble in the petroleum thinners used and of as high a degree of blackness as it is possible to obtain, consistent with the foregoing requirements. This for instance eliminates the soft asphalts, also the difficultly soluble asphalts such as elaterite and similar products. The requirements as to blackness and toughness, as well as complete solubility in the finished and cooled Japan, eliminate many of the stearine pitches.

The genuine asphaltums have a brown to brownish black "streak," a fixed carbon content of 15 per cent to 20 per cent, and are entirely unsaponifiable. The bone pitches are intensely black, have a fixed carbon content of 20 per cent to 25 per cent and are only slightly soluble in petroleum thinners, a considerable percentage of oil or coal tar thinner being required to keep them in solution in a Japan. They usually contain from a trace to 15 per cent of saponifiable matter. The desirable stearine pitches are fairly black in color, have a fixed carbon content of 5 per cent up to occasionally 10 per cent and have a considerable percentage of saponifiable matter, occasionally as high as 65 per cent. In admixtures the stearine pitch "break" imparts a certain degree of softness or approach to a rubber-like consistency according to the percentage present.

Blown petroleum residuums and pitches offer more serious difficulties, as they constitute a wide range of products of somewhat diverse characteristics. They are all unsaponifiable, and the more solid products re-



main largely with the break while the more liquid residuums remain in the pentane soluble portion and are distinguished from the soluble stearine pitch by being neutral and having a very low iodine value, whereas the soluble stearine pitch has a considerable acid value, a considerably higher iodine value and is partially saponifiable.

The fossil resins will remain almost wholly and rosin only partially with the "break." Their detection and estimation will be discussed in a subsequent paragraph.

**254. Comparative tests.** It is therefore necessary for the analyst to prepare a series of black Japans containing one gum only and also typical admixtures. These blacks should be prepared in the usual manner except that they do not contain the volatile thinner. The percentage of "break," the "streak" or blackness of the "break" when rubbed out on a sheet of unglazed white paper or porcelain, the hardness, and the percentage of fixed carbon of each should be carefully determined. From the data thus obtained it is a comparatively easy matter to fuse together weighed amounts of the individual breaks and test the resulting mass for blackness, consistency, and fixed carbon content, repeating the procedure until a product is obtained that corresponds to the sample under examination.

It should be remembered that whereas only about 70 per cent of the asphaltum and of the stearine pitch is precipitated by the pentane, 90 per cent or better of the bone pitch is precipitated, but when in admixture with considerable percentages of linseed oil and stearine pitch it becomes somewhat more soluble and only about 80 per cent breaks out. Iron and man-

ganese linoleates present in the Japan as driers affect the consistency of the "break," making it less friable. The quantity however is usually quite small and can be calculated from the percentage of iron and manganese found in the ash from incinerating the "break" after deducting the amount of iron normally present in "break" of the gums used.

**255. Fixed carbon.** Occasionally a heavily oxidized oil may be present and be precipitated with the gum break, giving it a somewhat rubber-like consistency and a lower fixed carbon value. If there is reason to suspect the presence of such oil and also if fossil gums or rosin be suspected, the break may be saponified, the unsaponifiable removed with benzol and the oil acids and the gum acids in the aqueous solution separated and estimated by esterification as described in Chapter XIX, Analysis of Varnish and Enamel Liquids.

The following table gives the fixed carbon content of representative gums and other products as determined by the author.

TABLE XXVII

TYPICAL ANALYSES	
Product	Fixed Carbon Per Cent
Stearine pitch, natural.....	6.6
“ “ after a normal cook.....	8.0
“ “ break.....	8.3
Gilsonite, natural.....	17.0
“ break.....	18.4
Bone pitch, natural.....	21.0
“ “ break.....	24.0
Heat-treated linseed oil.....	0.6
"Break" from baking Japan.....	14.6
Duplicate "break" of same blackness and consistency obtained by melting together the component breaks.....	14.1

**256. Calculation.** Having ascertained the percentages of component breaks which, when melted to-

gether, give the closest approximation to that obtained from the Japan under examination, as to blackness, consistency, and fixed carbon content, and also having established the extent to which each of these cooked gums will be precipitated by the pentane treatment, the total percentage of gums present in the Japan may be readily calculated.

## EXAMPLE

Percentage of "break" or insoluble gums 23.8 per cent.

Percentages of component "breaks" required to duplicate

54 per cent stearine pitch having a break coefficient of 70

38 " " gilsonite " " " " " 69

8 " " bone pitch " " " " " 80

Calculated "break" coefficient = 70 approximate;

$(23.8 \div 70)100 = 34$  per cent total gum content;

$34 - 23.8 = 10.2$  per cent soluble gums.

Product	Ratio of Gums in Break	Break Co-efficient	Calc. Ratio of Gums in Japan	Percentage on Basis of Total Gum Content
Stearine pitch....	54	70	77	54
Asphaltum.....	38	69	55	39
Bone pitch.....	8	80	10	7

The accuracy of the above calculations is checked against the analysis of the portion reserved for the estimation of oil, i.e., the pentane soluble residue from the "break." If a serious discrepancy is found to exist, petroleum pitch or other uncommon components or an unusual manufacturing practice may be sus-

pected and the procedure will have to be developed accordingly. Unless the petroleum residuum or pitch is of an unusual nature its presence and an approximate idea of the amount present may be ascertained by determining the percentage of saturated hydrocarbons and of free asphaltous acids in the break as described by Abraham in his treatise on Asphalts and Allied Substances, page 298, and comparing the results obtained with those from Japans of known composition containing such petroleum products as the base.

Occasionally a crude coal tar distillate may have been used as one of the solvents, especially if a bone pitch is present. Not all of this product will be removed by the steam distillation and this fact must be taken into consideration when testing for the possible presence of coal tar pitches by the well-known diazo and anthraquinone reactions.<sup>1</sup>

**257. Estimation of oil.** Five grams of the oil and pentane soluble gum residue, obtained as previously described, are saponified in the usual manner and the percentage of unsaponifiable determined. It is preferable to use benzol instead of ether as the extracting agent. If an emulsion forms that refuses to break, add more benzol to a total of about 500 c.c. and then 100 c.c. of ethyl alcohol, and allow to stand in a warm place overnight.

The percentages of saponifiable in the pentane soluble part of representative cooked stearine pitches are established. Therefore the percentage of unsaponifiable plus the calculated percentage of saponifiable due to the stearine pitch present subtracted from the total of the oil and soluble gum residue gives the approximate percentage of oil present. To

<sup>1</sup> Abraham, Asphalts and Allied Substances, pages 549-550.

this percentage should be added the small percentage of oil combined with the manganese and iron in the "break" portion as previously discussed. The acid soaps in the aqueous solution may be recovered and after liberation of the free acid may be esterified for the separation of any rosin or resin not precipitated by the pentane treatment. The acid value and Liebermann-Storch reaction of the recovered gum acids indicate their source.

**258. Acid Value.** Heat 5 grams of the soluble portion with 50 c.c. of alcohol on the steam bath for 30 minutes under an air condenser with frequent shaking. Decant from the insoluble residue while hot and extract the residue twice more with alcohol in the same manner. Combine the 3 extracts, cool, add 10 c.c. of a nearly saturated barium chloride solution, use phenolphthalein as the indicator and titrate with tenth-normal aqueous potash. A blank should be run on the alcohol. A high acid value may indicate stearine pitch in quantity, or a low grade of fish oil, samples of which have been examined by the author with acid values as high as 60, whereas the acid value of the linseed oil developed in the cooking of the Japan seldom exceeds 20.

**259. Iodine value.** The iodine values of the oil and soluble gum portion, of the unsaponifiable obtained therefrom and of the fatty acids obtained from the saponifiable throw considerable light on the probable composition, especially when compared with the values obtained from heat-treated oils, their fatty acids and the iodine values of the saponifiable and unsaponifiable portions of representative cooked pitches.

**260. Oils used.** Formerly linseed oil was the only oil used in baking Japans; at the present time fish



oils, chiefly menhaden, soya-bean oil, perilla oil, and occasionally a small percentage of tung oil, as well as linseed oil are being used. Inasmuch as the heat treatment they receive varies with the requirements of the Japan and also according to the ideas of the varnish maker, it is impossible to identify the oils used by analysis. In the absence of stearine pitch a rough approximation may be arrived at by the constants of the recovered fatty acids.

**261. Fixed carbon value of oil portion.** The composition of the oil and soluble gum portion is further confirmed by determining its fixed carbon value and comparing with the fixed carbon value of the pentane soluble parts of cooked oils, asphaltums and stearine pitches, a few typical values being given in accompanying table.

TABLE XXVIII

## TYPICAL FIXED CARBON VALUES

Product	Fixed Carbon Per Cent
Asphaltum, soluble.....	14.0
Stearine pitch, soluble.....	1.2
Treated linseed oil .....	0.6
Oil portion from baking Japan.....	3.5

**262. Estimation of metallic driers.** The iron and manganese are determined in the usual manner from a suitable quantity of ash obtained by incinerating a weighed quantity of the Japan. Frequently the ash is so light that the air currents from the flame used will carry away an appreciable amount. This can be avoided by cooling the crucible and moistening the ash with a few drops of water and then reheating. From the total quantity of iron obtained must be deducted the amount normally present in the gums used, which is quite appreciable. The corrected percentage of iron and the manganese are calculated to

the corresponding linoleates. The author knows of no way of determining whether the iron obtained is derived from Prussian blue or from a prepared iron soap which is the more recent practice. If lead is present it is best estimated as in the preceding chapter, using sulphuric and perchloric acids.

**263. Conclusion.** In order to obtain concordant results, the analytical procedure as to quantities, concentration, temperatures, etc., must be kept strictly comparative as regards the sample under examination and in establishing the necessary data from products of known composition. In order to properly interpret the results obtained the analyst must have a broad, comprehensive knowledge of the raw materials used and the prevailing manufacturing practice.

## CHAPTER XVIII

### ANALYSIS OF SHELLAC AND LACQUERS

**264. Valuation.** The analytical examination of shellac and shellac varnishes has been carried out much more extensively in recent years, owing to the improved chemical methods available for determining adulteration. The value of commercial shellac is dependent upon several conditions, chiefly its color, its freedom from dirt, as well as its content of added rosin, and in the case of bleached shellac, the moisture content and its ready solubility in alcohol. With shellac varnish, the kind and proof of the solvent used, the percentage of rosin or other substitutes if any, and the percentage of shellac present are the determining factors in its valuation.

**265. Determination of the body of shellac varnishes.** Three to five grams of the well-stirred sample are weighed into a weighed flat-bottom Petri dish and evaporated to a constant weight in the steam oven. The result is calculated in pounds per gallon. If a platinum evaporating dish be used and the evaporation conducted over a water bath, the amount taken should not be over 1 gram. Taking the weight of a gallon of alcohol at 60° F. as 6.75 pounds, the pounds per gallon may be ascertained by means of the following table:

TABLE XXIX

Per Cent Residue	Pounds Per Gallon
30.77.....	3.0
34.15.....	3.5
37.20.....	4.0
40.00.....	4.5
42.55.....	5.0
44.90.....	5.5
47.06.....	6.0
49.05.....	6.5
50.91.....	7.0
52.63.....	7.5
54.23.....	8.0

**266. Examination of the solvent.** One hundred grams of the varnish are carefully distilled at a moderate temperature, using an oil bath and a distilling bulb of the type described in Chapter XIII, collecting the distillate in a cooled flask with as little exposure to the air as possible. The proof of the solvent is determined from its gravity. If the solvent is recovered from a bleached shellac varnish its proof will be somewhat lower than when originally used, due to the residual water in the bleached shellac.

**267. Detection of rosin — Liebermann-Storch reaction.** About 1 gram of the sample is dissolved in about 15 c.c. of acetic anhydride, warming gently until the solution is complete. Cool thoroughly under the tap. The rosin will remain in solution while the greater part of the shellac will separate out. Filter. Place a few drops of the filtrate on a porcelain crucible, cover, and add by means of stirring rod one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin is present a characteristic violet fugitive color results. A pure shellac should give no coloration.

According to Hicks<sup>1</sup> this reaction is not very sen-

<sup>1</sup> Eighth International Congress of Applied Chemistry, Vol. XII, p. 115.

sitive, its limit for rosin in shellac being about 2 per cent, that is to say, shellacs yielding Wijs iodine values below 22-24 may not give a positive reaction when this test is applied. He recommends the Halphen test as much more sensitive and reliable.<sup>1</sup>

**268. Halphen test.** The Halphen reagent consists of two solutions: (a) 1 part by volume of phenol dissolved in 2 parts of carbon tetrachloride and (b) 1 part by volume of bromine in 4 parts of carbon tetrachloride.

The procedure which was found most convenient for conducting the test is as follows: A small quantity of the powdered resin, or the residue resulting from the evaporation of the ethereal extract of a larger quantity of the substance to be investigated, is dissolved in from 1 to 2 c.c. of solution A. This solution is poured into one of the cavities of an ordinary porcelain color-reaction plate until it just fills the depression; a portion of the solution will soon be seen to spread out on the flat part of the plate a short distance beyond the rim of the cavity, unless too much of the carbon tetrachloride has been lost through evaporation during the process of solution, when a drop or two more should be added to produce the spreading effect above referred to. Then immediately in an adjacent cavity of the plate a c.c. or so of solution B is placed and the bromine vapors evolved are allowed to impinge upon the surface of the solution in the other cavity. Sometimes it is necessary to blow a gentle current of air in the proper direction to accomplish this satisfactorily, or both cavities may be covered by a watch crystal of suitable size.

The color reactions begin almost immediately with

<sup>1</sup> Hicks, J. Ind. and Eng. Chem., Vol. 3, No. 2 (1911).



the contact of the bromine vapors and are best observed upon the flat portion of the test-plate. In most cases they last long enough for satisfactory observation; the changes in colors are practically over, however, in a period varying from five to ten minutes.

The author has found this method very satisfactory where rosin was the only adulterant; where the rosin is in admixture with other gums, as may be the case in the various substitutes now offered to the trade, this method has not proven satisfactory.

**269. Preparation of sample for estimation of rosin.** If much rosin is present, it is not safe to take the residue after evaporation for the quantitative estimation as has been shown by Langmuir. "A little rosin (iodine value 224.3) was dissolved in alcohol, evaporated on the water bath and heated 5 hours. It then showed a value of 148.2. Similarly, a dark rosin 175.5 fell to 131."

A quantity of the varnish sufficient to yield 0.2 to 0.4 gram of residue is weighed from a small vial, provided with a perforated stopper carrying a shortened 1 c.c. pipette, into a 200-c.c. Erlenmeyer flask; the weight of the sample used being thus obtained by difference. The sample in the flask is carefully evaporated at a low temperature until very pasty and then dissolved in the requisite amount of acetic acid and chloroform and the iodine number then determined as described in the following sections. The error due to the action of the small amount of alcohol remaining in the pasty mass on the thiosulphate is negligible.

**270. Determination of rosin in shellac as prescribed by American Society for Testing Materials.<sup>1</sup>** Solutions required. The solutions required are one of

<sup>1</sup> A. S. T. M. Standards, 1918, page 610.

iodine monochloride containing 13 g. of iodine per liter, in glacial acetic acid that has a melting point of 14.7 to 15° C. and is free from reducing impurities; and another of sodium thiosulphate, made by dissolving 24.83 g. of the pure salt in a liter of water. In addition to these solutions there is required a quantity of acetic acid of the same strength as that used for making the solution of iodine monochloride. Pure chloroform and starch are also necessary.

**271. Iodine monochloride.** The preparation of the iodine-monochloride solution presents no great difficulty, but it shall be done with care and accuracy in order to obtain satisfactory results. There shall be in the solution no sensible excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary. Set aside a small portion of this solution, while pure, and pass dry chlorine into the remainder until the halogen content of the whole solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged, there will be a slight excess of chlorine, which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

**272. Method.** Introduce 0.2 g. of ground shellac into a 250-c.c. dry bottle of clear glass with a ground-glass stopper, add 20 c.c. of glacial acetic acid (melt-

ing point  $14.7$  to  $15^{\circ}\text{C.}$ ) and warm the mixture gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble; solution is quicker according to the proportion of rosin present. Add 10 c.c. of chloroform and cool the solution to  $21$  to  $24^{\circ}\text{C.}$  The temperature should be held well within these limits during the test. Add 20 c.c. of Wijs solution from a pipette having a rather small delivery aperture. Close the bottle, place in a dark place, and note the time. It is convenient to keep the bottles during the test partly immersed in water which should be kept as nearly as possible between  $22$  and  $23^{\circ}\text{C.}$

Pure shellac will scarcely alter the color of the Wijs solution. If in small amount, rosin will produce a slowly appearing red-brown color. In large amount, rosin causes an immediate coloration, increasing in intensity as time passes. After 1 hour, add 10 c.c. of 10 per cent potassium-iodide water solution. Titrate the solution immediately with the sodium-thiosulphate solution; 25 or 30 c.c. may be run in immediately, unless the shellac is very impure, and the remainder gradually, with vigorous shaking. Just before the end, add a little starch solution. The end point is sharp, as the reaction products of shellac remain dissolved in the chloroform; any color returning after half a minute or so is disregarded.

**273. Blank.** A blank determination should be run with 20 c.c. of Wijs solution, 20 c.c. of acetic acid, 10 c.c. of chloroform, and 10 c.c. of 10 per cent potassium-iodide solution. The blank is necessary on account of the well-known effect of temperature changes on the volume, and possible loss of strength of the Wijs solution.

**274. Adulterated samples.** In the case of grossly adulterated samples, or in the testing of pure rosin, it is necessary to use, instead of 0.2 g. of material, a smaller amount, say 0.15 g. or even 0.1 g., in order that the excess of iodine monochloride may not be too greatly reduced, since the excess of halogen is one of the factors in determining the amount of absorption. In case less than 25 c.c. of the thiosulphate solution are required, another test should be made, using a smaller amount of the shellac to be tested.

**275. Weighing.** In weighing shellac, some difficulty is at times experienced on account of its electrical properties. In very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it, and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

**276. Calculation.** No pure shellacs show a higher iodine absorption than 18. As shellac is relatively a high-priced material and as the variation between its highest and lowest figure is not great, it is recommended that 18 should be taken as the standard figure for shellac, determined by the method above described.

As it is an accepted principle that a standard method should be so devised that its inaccuracies shall work in the direction of favoring the seller rather than of condemning too severely the article sold, it is recommended that the value for the iodine number of rosin be taken as 228. The result of using in this method the value 18 as the iodine number of shellac and 228 as the number of rosin, may be that a slightly lower percentage of rosin, under some circumstances, will be found than that which is actually present.

The percentage of rosin is determined as follows:

$$\begin{array}{rcl}
 \text{Iodine number of shellac} & = & 18 \\
 \text{Iodine number of rosin} & = & 228 \\
 \text{Iodine number of mixture} & = & X \\
 \text{Percentage of rosin} & = & \frac{(X - 18)}{(228 - 18)}
 \end{array}$$

**277. Insoluble test for shellac.<sup>1</sup>** The separation of the soluble from the insoluble portion of the lac is

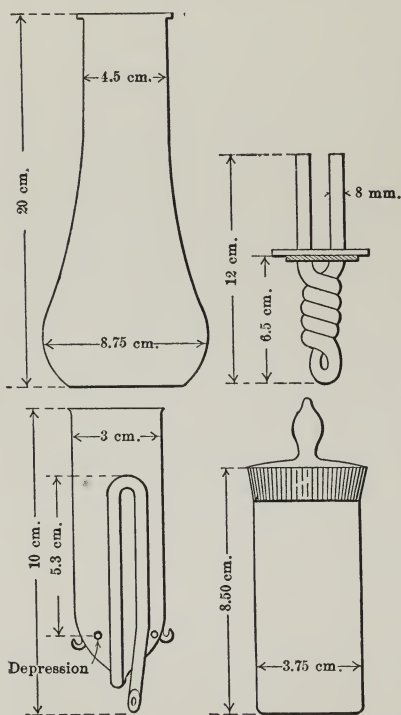


FIG. 8.—APPARATUS FOR THE INSOLUBLE TEST FOR SHELLAC

made by extracting approximately 5 g. of the lac in a paper cartridge, which is held in a tube provided with a siphon as in the Knoefler extraction apparatus, and is heated by the vapors of the alcohol which pass around the tube and are then condensed by a return condenser to fall as liquid upon the shellac to be extracted. The siphon tube should be slightly larger than the cartridge, which should be supported so that it does not rest directly on the bottom.

**278. Apparatus.** The most convenient apparatus for carrying out the process is illustrated in Fig. 8. It consists of a wide-neck flask in which is suspended a metal return condenser. From the lower part of this condenser is hung a siphon tube of the Knoefler

<sup>1</sup> A. S. T. M. Standards, 1918, p. 612.



type. A Schleicher and Schuell extraction cartridge, No. 603, 26 mm. in diameter by 60 mm. high, is used in a siphon tube of such a size that the top of the cartridge is just above the upper curve of the siphon, the paper thimble being cut down if necessary. It is supported on three indentations in the glass so that there is a little space underneath and around the cartridge to allow of a free flow of liquid. To insure the complete extraction of all matters soluble in alcohol in the cartridge itself, it should be thoroughly extracted with 99.5 per cent methyl alcohol before use. Then place the cartridge in a glass-stoppered weighing bottle and dry to constant weight in an air bath at 100° C.

**279. Procedure.** Place a sample of approximately 5 g. of the pulverized lac in the cartridge, and transfer to the extraction apparatus. Fill the cartridge with cold alcohol of the character described to a point just below the upper curve in the siphon. The cold alcohol is allowed to act upon the lac for 1 hour before the extraction commences.

Keep the alcohol boiling briskly during the extraction. The rate of extraction may be controlled by the use of an electric stove of the Simplex type, 4½ in. in diameter, and using the full current of 2.2 amperes at 110 volts. The volume of methyl alcohol in the flask should be 125 c.c., in addition to the alcohol required to fill the siphon. Protect the flask from drafts. Under these conditions the tube will siphon over about 33 times in 1 hour. The condenser should be able to return all the alcohol volatilized during the vigorous boiling of the contents of the flask, the object being to effect the maximum extraction during the specified time.

**280. Time.** The color is removed by the end of the first hour in practically every case and in order to eliminate any variations due to difference of opinion as to the exact time when the color has disappeared, the total extraction period shall be limited to exactly 2 hours, time being taken from the moment when the first siphon tube of alcohol has passed over. After extraction, place the cartridge in the weighing bottle, dry to constant weight at 100° C. and weigh.

**281. Calculation.** The weight of the residue insoluble in alcohol thus obtained, divided by the weight of the sample, and this quotient multiplied by 100, is the percentage of alcohol-insoluble matter in the lac.

**282. Cautions to be observed.** It will be noted that there are three depressions in the lower part of the glass extraction thimble to hold the cartridge above the bottom. This is very necessary for the reason that during the early part of the extraction, a very free flow must be maintained to prevent the blocking of the siphon with the wax, which, though readily soluble in hot alcohol, is with difficulty soluble in cold alcohol. The object in filling the cartridge with cold alcohol, before starting the extraction proper, is to allow the resin and some of the wax to dissolve at a low temperature. If the higher temperature of the boiling alcohol were immediately applied it would fuse the resin into a lump and render the extraction difficult. The first few drops of distilled alcohol which fall into the cartridge will cause the extract to siphon over, thus eliminating the bulk of the resin at the start.

**283. Determination of moisture in bleached shellac.<sup>1</sup>** Both orange and bleached shellac give off vola-

<sup>1</sup> A. S. T. M. Standards, 1918, page 615.

tile matter at temperatures approaching 100° C. Bleached shellac alters chemically at these temperatures, losing its solubility in alcohol. For these reasons the usual methods of determining moisture by heating in the air bath at 100 to 110° C. are not applicable in the analysis of shellac.

**284. Sampling.** Bleached shellac is sold in three forms, as hanks or bars containing approximately 25 per cent of water, as ground bleached in pulverized form with about the same water content, and as bone-dry or kiln-dried shellac. The latter is prepared by drying the ground-bleached shellac in the air or in vacuum driers at moderate temperatures. It may contain, depending upon the completeness of the drying and weather conditions, up to 10 per cent or more of water.

In sampling bone-dry or kiln-dried bleached shellac, a fairly large portion (about 1 lb.) should be taken from different parts of the barrel and finely ground by running quickly through a coffee mill. No attempt shall be made to sieve it. It shall be rapidly mixed and transferred to a Mason jar provided with a screw cap and rubber ring seal. The jar should not be more than two-thirds full, leaving room for a thorough mixing by shaking the contents. It shall be kept in a cool place and tested as promptly as possible. If too warm the shellac may become partly caked, in which case the lumps shall be broken up by shaking the bottle.

In sampling bars or hanks it is recommended that a whole hank be taken. It should be crushed and ground as rapidly as possible. Ground-bleached shellac may be treated as above, bearing in mind that the large amount of moisture present makes rapid handling imperative.

**285. Method No. 1.** Weigh from 5 to 10 g. of the sample in flat-bottom dishes about 4 in. in diameter or in watch glasses ground to fit and provided with a clamp. Spread out the contents of the dish in a thin layer to expose as large a surface as possible. Place the shellac in a desiccator freshly filled with concentrated sulphuric acid. Exhaust the desiccator by a vacuum pump as completely as possible. With a good vacuum (3 mm. pressure or better) constant weight will be obtained in between 24 and 48 hours.

Absolutely dry shellac is quite hygroscopic and the final weight should be taken as rapidly as possible.

**286. Method No. 2.** The same results may be obtained by drying the shellac in a well-ventilated air bath from 3 to 6 hours at 100 to 110° F. (38 to 43° C.). One or two electric light bulbs provide a convenient source of heat. The temperature should not be allowed to rise above 43° C., otherwise sintering may occur and retard drying. With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight.

It is recommended that analysts check the accuracy of results obtained in the oven by comparison with a test made in a vacuum desiccator before relying exclusively on the oven.

**287. Insoluble test.** When the determination of alcohol insoluble matter in bleached shellac is required, the sample shall be dried if in the form of bars or ground bleached, as the water present dilutes the alcohol to a point where solution may not be complete. Prolonged heating at the temperatures of 38 to 43° C. stated above may render the shellac partly insoluble, and it is recommended that in preparing shellac for



this determination a separate portion be dried by exposure to the air in a thin layer, without the application of heat.

**288. Substitute shellacs.** Owing to the comparative high price of shellac, innumerable combinations of other gums and products aside from rosin have appeared on the market. Manila cut with alcohol is the most common and the most widely used; it is easily recognized from its characteristic odor. It should be remembered that the chief use of shellac varnishes and shellac substitutes is for a "first coater," which is usually "sanded" and therefore the most important test to be applied to such substitutes is to ascertain if they can be satisfactorily "sanded" without gumming the paper. Very few substitutes will pass this test, which is the reason why most of them disappear from the market in a short time.

**289. Lacquers.** The manufacture of lacquers is an industry in itself and until recently has been developed apart from the paint, enamel and varnish industries. Recent industrial developments have shown that there is a big field for lacquers and numerous paint and varnish concerns have taken up their manufacture. Owing to the wide variety of solvents, gums and other components which may be present in any particular lacquer, it is impossible to present a detailed procedure that would be satisfactory under all circumstances. The proximate Analysis of Nitrocellulose Solutions and Solvents by Conley, J. Ind. Eng. Chem. 7, p. 882, and Analysis of Zapon and Celluloid Lacquers by Zimmer, Kunststoffe 3, p. 324, present definite outlines for the examination of cellulose products which the author believes will be found satisfactory in the majority of cases.



## CHAPTER XIX

### ANALYSIS OF VARNISH AND ENAMEL LIQUIDS

**290. Difficulties to be encountered.** The author does not believe that a purely analytical procedure can be developed for the analysis of a varnish that will prove reliable, which has for its purpose the duplication of the varnish or its correct valuation.

A procedure, however, can be developed which, in the hands of a chemist familiar with the different gums used and the different processes and details of varnish manufacture, with extensive analytical data obtained from varnishes of known composition, will prove satisfactory for valuation and duplication. Several such schemes are now in use by varnish chemists with satisfactory results. The scheme outlined herewith has been developed and used by the author for several years with excellent results and its practical value is becoming increasingly greater with the increasing volume of comparative data that is being established. For obvious reasons the author cannot present in this connection the comparative data he has established, or certain exact details of manipulation as they are based on the varnish formulas and procedure of certain corporations or are derived from other confidential sources of information.

**291. Determination of volatile thinner.** The percentage of volatile oils present and their characteristics are best determined by following the procedure given in Chapter XIII.

**292. Determination of metallic driers.** The metallic driers present are determined as in Chapter XVI beginning with section 226. If the vehicle has been extracted from an enamel or color varnish it will usually be found that it will also contain, either in combination or held mechanically, a small percentage of the pigments used. Zinc and lead pigments especially enter into combination with the vehicle (see Chapter XV). Incineration invariably gives an ash which will be materially low as to lead content. V-39

**293. Separation of oil and resin.** If it is desired to determine only the total percentage of oil and of gum, and no examination is to be made of the nature of each, 5 grams only of the varnish need be taken with a corresponding reduction in the amounts of alcoholic sodium hydroxide and ether, and unless it is a very quick drying varnish, or grinding Japan, the carbon dioxide treatment can be omitted. V-41

If the character of the oil and gum acids is to be determined the following procedure is followed. Weigh by difference about 10 grams of the varnish into a 250-c.c. Erlenmeyer flask, add about 50 c.c. water and boil, using an oil bath at a moderate heat until the contents of the flask (uncovered) have been reduced to a total of about 15 c.c. as nearly as can be judged. A moderate stream of carbon dioxide gas should be passed into the flask to prevent oxidation during the evaporation, 50 c.c. more of water is added, and the evaporation again repeated in an atmosphere of carbon dioxide to a volume of about 10 c.c. This will remove practically all of the volatile thinner. Occasionally a heavy solvent may be present and a small percentage of the high boiling point petroleum fractions will remain. The allowance to be made and

deducted from the unsaponifiable is determined from comparative data after the volatile thinner obtained as described in section 173 has been distilled. If the product is a grinding Japan or an especially quick drying varnish, the carbon dioxide treatment must be conducted very efficiently to prevent oxidation.

**294. First saponification.** Add 100 c.c. of  $\frac{N}{2}$  alcoholic sodium hydroxide and boil under a reflux condenser for 3 hours. With some varnishes it may be necessary to use 15 to 25 c.c. C. P. benzole when saponifying. Evaporate to a bulk of about 20 c.c.

Transfer to a separatory funnel, using a policeman if necessary, washing the flask thoroughly with water and sulphuric ether. Dilute to about 200 c.c. with warm water and shake until the soaps have dissolved. Cool and add 200 c.c. sulphuric ether and shake thoroughly, but carefully, with a circular motion so as not to form an emulsion unduly difficult to break up. It is best to arrange the work so that this point is reached later in the afternoon, so that the separation may take place overnight. If an emulsion forms which does not break down or if it is necessary to hasten the separation, alcohol in 2 c.c. portions may be added, using a pipette and introducing the alcohol into the emulsion portion.

**295. First unsaponifiable.** Draw off the aqueous solution into a larger separatory funnel and wash the ether solution 4 times with small amounts of water, adding the washings to the aqueous solution in the large funnel. It is advisable to use a specially arranged ring stand which will support in the proper positions all the separatory funnels that are used in the entire separation, as considerable time is saved thereby.

Draw off the ether solution which contains part of the unsaponifiable into a weighed flask and set aside until later in the analysis.

**296. Recovery of mixed oil and resin acids.** Acidify the aqueous solution with hydrochloric acid and extract 4 times with ether, using about 40-c.c. portions. Wash the combined ether portions 4 times with water. Discard the aqueous solution and aqueous washings.

Transfer the ether solution to a 150-c.c. Erlenmeyer flask and distill off the ether, using an oil bath heated by an electric hot plate. When the bulk of the ether has been removed, uncork the flask and continue the evaporation with the flask open and with an atmosphere of carbon dioxide. Finally use two 10-c.c. portions of *absolute* ethyl alcohol to remove the last traces of moisture. Not only is it necessary to prevent oxidation but the temperature must not exceed 105° C. in order to prevent polymerization of tung oil acids, which may be present. If the moisture is not completely removed, the esterification which is the next step will not be sufficiently complete.

**297. Esterification.** The esterification can be conducted according to the well known Twitchell method with very careful attention to detail, using hydrochloric acid gas that has been carefully dried. The author has found Wolff's method<sup>1</sup> equally efficient and much more rapid and satisfactory. Dissolve the residue in 40 c.c. absolute alcohol and add 40 c.c. of a mixture of 1 part conc. sulphuric acid to 4 parts absolute alcohol. Heat quickly to boiling and boil for 4 minutes under a reflux condenser. If absolute ethyl alcohol is used great care must be taken to preserve it and the acid-alcohol mixture from absorbing mois-

<sup>1</sup> Chem. Ztg., 38, pages 369-370, 382-383.



ture. To avoid these difficulties the author has used absolute methyl alcohol, using only the best procurable grade.

Completely transfer the contents of the flask at once to a separatory funnel, washing the flask with ether and water, add 150 c.c. ether, and after agitation add 100 c.c. of a ten per cent solution of sodium chloride. Draw off the aqueous portion, repeat the extraction with two successive 50-c.c. portions of ether. Discard the aqueous solution and wash the combined ether portions twice with water and discard the aqueous washings.

**298. Separation of fatty acid esters from resin acids.** To the ether solution add 100 c.c. of  $\frac{N}{5}$  aqueous sodium hydroxide. Shake thoroughly and allow to separate, then repeat the shaking. After separating draw off the aqueous solution into another separatory funnel. Wash the ether solution twice with 75 c.c. water containing 5 c.c. alcohol and 5 c.c. of the  $\frac{N}{5}$  sodium hydroxide. Add these washings to the main aqueous solution.

The ether solution contains the methyl or ethyl esters of the fatty acids, depending on the alcohol used, and part of the unsaponifiable. The aqueous solution contains the resin acid soaps. If insoluble soaps are formed when the ether solution is treated with the  $\frac{N}{5}$  sodium hydroxide they are to be carried along into the final resin soap solution.

**299. Resin soaps.** Extract the aqueous resin soap solution with two 75-c.c. portions of ether and add



to the main ether solution and wash the combined ether portions with water. The combined aqueous solution and washings are preserved in a separatory funnel for the subsequent liberation of the resin acids.

**300. Second saponification.** The ether solution containing the esters is transferred to a small Erlenmeyer flask and the ether distilled off, using the same procedure as in section 296 except that the final traces of moisture need not be removed with alcohol. To the residue are added immediately 50 c.c.  $\frac{N}{2}$  alcoholic sodium hydroxide and boiled under a reflux condenser for 45 minutes.

Evaporate rapidly from open flask on electric hot plate to a bulk of approximately 15 c.c., dilute with 100 c.c. warm water, and transfer to separatory funnel, rinsing flask with water and ether. Cool, extract four times with ether and wash the combined ether extract thoroughly with small portions of water. These aqueous washings are added to the main aqueous solution. This solution contains the soaps of the fatty acids.

**301. Second unsaponifiable.** The combined ether extract from preceding section contains the balance of the unsaponifiable and is added to the ether solution containing the first unsaponifiable (see section 295). The ether is distilled off, two 5-c.c. portions of absolute alcohol are added to remove all traces of moisture, heated carefully until all the alcohol has disappeared, cooled and weighed as total unsaponifiable. When the bulk of the ether has been distilled off, it is preferable to transfer to a 50-c.c. Erlenmeyer flask and the determination finished in this flask, as the flask has to be crushed for the identification treatment of the gums.

**302. Recovery of the oil acids.** The aqueous solution containing the soaps of the fatty acids is acidified with hydrochloric acid and extracted thoroughly with ether in the usual manner. Discard the aqueous portions. Transfer to a small Erlenmeyer flask, distil off the bulk of the ether, disconnect flask, introduce current of carbon dioxide, evaporate the remainder of the ether, add two 5-c.c. portions of absolute alcohol to remove traces of moisture, heat at  $105^{\circ}\text{C}$ . to constant weight in current of carbon dioxide. This temperature should not be exceeded or maintained longer than necessary because of its effect on the tung oil acids that may be present. The residue is weighed as the fatty acids and preserved in an atmosphere of carbon dioxide if an estimation of the tung oil acids is to be made. This weight of the fatty acids plus the weight of any oxidized fatty acids obtained in section 304 can be taken as equivalent to the weight of oil present in the varnish as a small percentage of the gum constituents remain with the oil acids and substantially compensate for the glycerine content of the oil.

**303. Recovery of the resin acids.** The aqueous solution of the resin acid soaps set aside from section 299 is acidified with hydrochloric acid and extracted with three 50-c.c. portions of ether, the combined ether portions washed twice with water and distilled, transferring completely to a weighed 50-c.c. Erlenmeyer flask after the larger part of the ether has been distilled. The last traces of moisture are removed with absolute alcohol and the evaporation carried out in an atmosphere of carbon dioxide at  $120^{\circ}\text{C}$ . to constant weight. This residue constitutes the resin acids which, plus the unsaponifiable (any petroleum residue

present having been deducted) multiplied by the proper factor determined by the nature of the gum acids, gives the amount of gum present in the varnish. Boughton<sup>1</sup> uses the empirical factor of 1.07. The flask containing the gum acids is preserved for subsequent examination as to their nature.

**304. Oxidized fatty acids.** Oxidized fatty acids do not esterify readily and if there is reason to believe that the varnish contains an oxidized oil in quantity or in case of doubt, the resin acids obtained in the preceding section should be given a second esterification following the procedure as previously stated beginning with section 297 and observing the same cautions. The weight of oxidized oils thus obtained should be added to the weight of acids recorded in section 302 and the resin acids after separation preserved for further examination.

**305. Sulphurized oils.** The use of sulphurized oils in paint and enamel vehicles is becoming increasingly common. Their presence can be detected and the approximate percentage present can be ascertained by determining the percentage of combined sulphur in the vehicle. Thoroughly sulphurized oils usually contain 6 to 7 per cent of combined sulphur, this amount being sufficient to produce a satisfactory "body," so that one part of oil will take one to two parts of volatile thinner and still have a medium consistency.

**306. Procedure.** Intimately mix by grinding in a mortar 0.5 gram of the nonvolatile portion of the oil, or 1 gram of the original oil with 3 grams of Eschka's mixture (2 parts light calcined magnesium oxide, sulphur-free, and 1 part dry sodium carbonate). Transfer completely to a porcelain crucible, cover with a

<sup>1</sup> Bureau of Standards, Technologic Paper No. 65, page 26.

layer of 0.5 gram of the Eschka mixture, and heat gently with an alcohol lamp near the top of the mixture. *No smoke must appear* and no darkening of the cover layer must occur. A gas flame cannot be used because it contains sufficient sulphur to affect the determination. Gradually rotate the crucible, so that all portions of the mass receive a uniform heating. After heating until dark particles do not appear on stirring, the contents are removed to a mortar and again finely ground, then transferred to a platinum crucible and again heated, but not above a very faint red for several hours. Cool, empty into a 300-c.c. beaker, digest on a water bath with 100 c.c. water for 30 minutes. Filter and wash the residue with four 20-c.c. portions of boiling water. Wash thoroughly on the filter.

Add 5 c.c. bromine water to filtrate, make just distinctly acid with hydrochloric acid, heat until the bromine is entirely expelled, precipitate with barium chloride solution in the usual manner. Filter, wash, ignite, and weigh as barium sulphate and calculate to S. A blank should be run on the Eschka mixture itself and such correction applied as may be necessary. If the room is free from sulphur compounds and the heating during the burning off is carefully regulated and is sufficiently low during the first part of the operation, accurate results can be obtained.

## CHAPTER XX

### ANALYSIS OF VARNISH AND ENAMEL LIQUIDS

(Continued)

**307. Separation of the oil acids.** A small portion should be taken and the iodine number determined as in the chapter devoted to tung oil. The balance is treated by the Ware-Schumann potassium soap method<sup>1</sup> as follows:

The oil acids, not exceeding 3 grams, are saponified with 100 c.c.  $\frac{N}{4}$  absolute alcoholic potash for 1 hour, the end of the return condenser being connected to a calcium chloride tube to prevent moisture absorption. The saponified mixture is cooled to 0° C., held for 10 minutes at that temperature, and filtered through a Gooch crucible, using a filter-paper disk instead of an asbestos pad. The precipitate, after washing thoroughly with ice-cold saturated absolute alcohol, is removed from the crucible to a cover glass, and is dried at 75 to 80° C., under vacuum. After cooling without removing from the desiccator, the precipitate is taken out and weighed, and the weight calculated to tung oil.

**308. Cautions to be observed.** It is necessary to use absolute alcohol both for saponification and for washing the precipitate, as the soap is appreciably soluble in the presence of even small amounts of water. This alcohol and alcoholic potash should be

<sup>1</sup> J. Ind. and Eng. Chem., Vol. 6, p. 806.



freshly saturated with the soap before use, for although the soap is but slightly soluble in absolute alcohol, that solubility changes on standing, especially if exposed to light. It is a comparatively easy matter to keep freshly saturated solutions ready for use by making up a batch of the soap and introducing it into the stock bottles of alcohol and alcoholic potash,

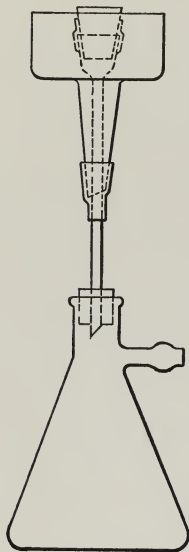


FIG. 9.

in quantities more than sufficient to saturate them at  $0^{\circ}\text{C}$ . When about to make a determination, the solution may be warmed until an appreciable amount of soap goes into solution, after which it may be cooled to  $0^{\circ}\text{C}$ . and held for 10 minutes and filtered. This fresh filtrate is ready for use.

During the washing of the precipitate the whole mass must be kept cold, for the solubility of the material in alcohol is greatly increased by a rise in temperature. This is accomplished by filtering through a Gooch crucible surrounded by cracked ice (see Fig. 9).

The precipitate is susceptible to oxidation and must be kept away from air during drying. Also, the fact that high temperature will char the soap limits the drying temperature to about  $80^{\circ}\text{C}$ .

The weight of potassium soap obtained is calculated to tung oil by comparing with the amount obtained from putting 3 grams of standard tung oil through the above treatment with alcoholic potash and with the same careful attention to detail.

**309. Separation of gum constituents.** The flask containing the weighed resin acids is crushed carefully

and very finely ground in a mortar with clean white sand. This mixture is placed in a cartridge and extracted for 24 hours with redistilled pentane (Standard Oil Co.), the higher boiling point portion of which has been discarded. The pentane is evaporated and the residue weighed.

The acid number of the residue is determined by dissolving in C. P. benzol and alcohol and titrating with alcoholic potash. A blank titration should also be run on the alcohol.

The neutral solution is acidified with hydrochloric acid, extracted with ether, and the resin acids submitted to further solubility tests with various aqueous alkaline solutions and other solvents, depending on the data already established. The flask containing the total unsaponifiable is crushed, ground with sand and given a similar extraction with the pentane.

**310. Identification of constituents.** Having established the percentage of unsaponifiable and of resin acids, the solubilities of each, the acid value of the original nonvolatile and of the resin acids, and comparing these results with data from numerous varnishes of known composition, the nature of the gums used and the treatment the oil portion has received can be determined with a fair degree of accuracy. This is based on the assumption that the analyst has an intimate knowledge of the different procedures used with the various gums and oils in varnish manufacture and has adequate data on the losses and changes that take place during their heat treatments.

Recently varnishes containing synthetic resins have appeared on the market. From the desirable qualities which these varnishes possess it is a fair assumption that they will have a wide usage in the near future.

These resins, which are of the cumarone type, are almost wholly unsaponifiable and therefore will be found in the first unsaponifiable (see section 295) and the varnish containing such resins will have a proportionally low acid value.

It should be remembered that the above described analytical procedure requires considerable quantities of ether almost continuously throughout the analysis and all due precautions should be adopted against fire and explosions.

**311. Kauri test for estimating percentage of oil.**

The percentage of oil in a varnish or enamel liquid can be determined with a fair degree of approximation without analysis by means of the Pulsifer Kauri Solution Test used in spec. 14,001-B, Spar Varnish Signal Corps, U. S. A. A series of varnishes of known composition are selected and the minimum amount of a suitable prepared oil is determined which is necessary to add to each, to enable it to just pass the specified bending test, after adding 50 per cent by weight of the kauri solution, the nonvolatile portion of the varnish plus the added oil being considered as 100 per cent. If the varnish or enamel liquid is very long in oil, no added oil will be necessary and the amount of kauri solution added is increased to the point where the mixture will just pass the bending test.

The varnish under examination is compared for body, drying, etc., with the above selected varnishes, the percentage of volatile is determined and a series of 3 or 4 tests made up by adding weighed amounts of prepared oil to the varnish as judged by the above comparison. One-half as much by weight of the kauri solution is added as the total of nonvolatile in

the varnish plus weight of added oil and the tests are completed as described herewith. The test which just passes the bending operation is the one to be used in calculating the percentage of oil present as compared with the varnishes of known composition.

### 312. Preparation of the Pulsifer kauri solution.

The kauri solution is made as follows: Arrange a distillation flask condenser (water cooled) and tared receiver for distillate on balance. Place in flask about  $\frac{1}{3}$  of its volumetric capacity of clean bright pieces of No. 1 kauri broken to pea size. Melt and distill carefully until 25% by weight is driven off. At the end of the distillation the thermometer in the distillation flask with bulb at the level of the discharging point of the flask should register approximately 700 degrees F.

Pour the residue into a clean pan—when cold break up and dissolve one part of the run kauri in two parts of pure spirits of turpentine by weight (at a temperature of approximately 300 degrees F.). This solution should be made in a carefully tared beaker and brought back to correct weight when cold by the addition of the amount of spirits of turpentine necessary to replace the loss by evaporation during the dissolving of the gum. If properly prepared all of the gum will remain in solution.

**313. Procedure.** Determine the nonvolatile content of the varnish under examination. Take 100 grams of the varnish and add to it an amount of the kauri solution equivalent to 50 per cent by weight of the nonvolatile plus weight of added oil. Mix carefully and thoroughly without warming. If for example 100 g. of the varnish contain 45 g. nonvolatile matter and 5 g. of oil are added, 50 grams of the kauri solution will be required.



Flow a coat of the varnish thus reduced on a tin panel of suitable size and weight ( $4 \times 5$  inches, 100-lb. tin). Allow to dry in a nearly vertical position at room temperature for one hour. Then place in an oven (at 200 to 212 degrees F.) in a horizontal position and bake for 5 hours at this temperature. Remove and allow to cool at room temperature (not less however than 70 degrees F.) for one hour.

Place the panel at a point approximately midway between the top and bottom edges (of the panel) over a  $\frac{1}{8}$ " rod (held firmly between suitable supports) and bend double rapidly. This bending should be done at a temperature not lower than 70 degrees F. and if possible not over 80 degrees F. The varnish, to pass the test, must show no cracking whatever at the point of bending. Cracking may best be detected by observing the bent panel held closely at the proper angle under a shaded artificial light using a magnifying glass.

With experience and adequate facilities the entire test can be run in one day and the results will be sufficiently accurate for most purposes.

**314. References.** The following references are of interest as they deal with various phases of varnish and enamel liquid analysis.

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## ADDENDA

### VOLUME EQUIVALENTS

1 liter	= 1000 cu. cm.
	= .03531 cu. ft.
	= 61.022 cu. in.
	= .2642 gal.
	= 2.202 lbs. water 15° C.
1 cubic centimeter	= .001 liter
	= .06102 cu. in.
	= .00026 gal.
	= .00022 lb. water 15° C.
1 cubic inch	= .0164 liter
	= 16.388 cu. cm.
	= .00433 gal.
	= .03608 lb. water 15° C.
1 gallon	= 3.785 liters
	= 3.785 cu. cm.
	= 231 cu. in.
	= 8.338 lbs. water 15° C.
1 liquid oz.	= 29.57 cu. cm.
1 liquid qt.	= 0.9463 liter
1 liter	= 1.0567 liq. qt.

### GRAVIMETRIC EQUIVALENTS

1 gram	= .03527 oz.
	= .0022046 lb.
1 ounce	= 28.35 grams
	= .0625 lb.
1 pound	= 453.6 grams

# INDEX

A	PAGE
Abel Pensky Tester.....	26
Acetate of lead.....	113, 138
Acetone, Messinger's method for.....	45
uses of.....	44
Acetone oils.....	46
distillation of.....	47
Agricultural paste paints.....	103
Air-drying Japans.....	154
Aldehyde-free alcohol.....	123
Aluminum, oleate.....	111
stearate.....	111
Asphaltums.....	158
characteristics of.....	158
fixed carbon of.....	161

B	
Baking Japans.....	154
analysis of volatile portion of.....	157
coal tar distillates in.....	163
estimation of gums in.....	158
estimation of metallic driers in.....	165
estimation of oil in.....	163
oils used in.....	164
volatile content.....	155
Benzol, distillation of.....	49
evaporation of.....	51
specific gravity of.....	49
uses of.....	49
Bleached shellac, moisture in.....	176, 178
insoluble test for.....	178
sampling of.....	177
Blown oils.....	77
Boiled oils.....	76
Bone pitches.....	158
Borate of manganese.....	138, 142
Borax.....	114
Browne's method.....	87

C		PAGE
Calcium . . . . .		153
Carbonate of soda . . . . .		113
Casein . . . . .		110
Caustic soda . . . . .		113
Centrifuge, use of . . . . .		98
Chinese Wood oil . . . . .		79
Chloride of lime . . . . .		112
Cobalt . . . . .		152
acetate . . . . .		138
resinate . . . . .		143
Copper . . . . .		146
Corn oil . . . . .		128
Cottonseed oil . . . . .		128
Cumarone resins . . . . .		191
D		
Denatured alcohol . . . . .		35
composition . . . . .		35
correction for temperature . . . . .		38
specific gravity of . . . . .		36
Determination of true red lead content . . . . .		139
Distemper colors . . . . .		104
Driers . . . . .		130
E		
Effect of emulsifying agents . . . . .		133
Effect of storage on drying oils . . . . .		136
Emulsifiers . . . . .		109
classification of . . . . .		110
effect of . . . . .		131, 133
need for . . . . .		131
Emulsion paints, deterioration . . . . .		110
F		
Fish oil . . . . .		92
determination of . . . . .		93
Foots . . . . .		61
estimation of . . . . .		62, 63
in South American seed . . . . .		63
Free asphaltous acids . . . . .		163
Free fatty acids . . . . .		123
iodine number of . . . . .		137
Free mineral acids in oils . . . . .		123
Ferrous sulphate solution, preparation of . . . . .		150

## G

## PAGE

Glue . . . . .	110
Glycerine . . . . .	112
Graining compounds . . . . .	104
Grinding oils . . . . .	77
Gravimetric equivalents . . . . .	196

## H

Halphen test . . . . .	169
Hanus' method . . . . .	58
Heckel's modification of Ford-Williams' method . . . . .	142
Hübls' method . . . . .	60
Hydrolysis, effect of . . . . .	76
of lead soaps . . . . .	132
of zinc soaps . . . . .	132

## I

Iodine monochloride . . . . .	171
Iodine number . . . . .	122
Iron linoleate . . . . .	151

## L

Lacquers . . . . .	179
Lead . . . . .	145
compounds of . . . . .	139
oleate . . . . .	111
stearate . . . . .	111
Liebermann-Storch reaction . . . . .	129, 168
Linseed oil, acid number of . . . . .	56
bodied . . . . .	77
constants of . . . . .	53, 63
density of . . . . .	55
fatty acids, preparation of . . . . .	65
flash point of . . . . .	124
foots . . . . .	64
from South American seed . . . . .	54
hexabromide number of . . . . .	65
iodine number of . . . . .	58
methods of testing . . . . .	54
refractive index of . . . . .	58
saponification number of . . . . .	56
specifications for . . . . .	53
specific gravity of . . . . .	54
unsaponifiable in . . . . .	57



Linseed oil, uses of . . . . .	52
Litharge . . . . .	138
Lumbang oil . . . . .	93

## M

Manganese . . . . .	146
Menhaden oil . . . . .	92, 128
analytical constants of . . . . .	93
Messinger's method . . . . .	45
Methyl acetate, estimation of . . . . .	46
Methyl alcohol, estimation of in mixtures . . . . .	42
Mineral oil . . . . .	125
estimation of . . . . .	126
Outerbridge test for . . . . .	127
separation from rosin oil . . . . .	126
Mineral spirits, War Department specifications for . . . . .	26

## N

Nitrocellulose solutions . . . . .	179
------------------------------------	-----

## O

Obtaining uniform sample . . . . .	96
Oils, oxidation of . . . . .	102
Oxide of manganese . . . . .	138
estimation of . . . . .	141
Oxidized fatty acids . . . . .	187
Oxygen absorption of oils . . . . .	129

## P

Paint, puttied . . . . .	134
Perilla oil . . . . .	94
Permanganate solution . . . . .	149
Petroleum pitches . . . . .	158
blown . . . . .	159
Petroleum thinners, distillation of . . . . .	14, 15, 20
temperature corrections for . . . . .	5
color of . . . . .	2
odor of . . . . .	1
solvent strength of . . . . .	2
specific gravity of . . . . .	3
Phosphate of soda . . . . .	114
Pine oil . . . . .	31
analysis of . . . . .	33

	PAGE
Pine oil, distillation of . . . . .	33
in petroleum products . . . . .	33
water in . . . . .	32
Pulsifer test . . . . .	192

## R

Reactions in paint on storage . . . . .	133
Red lead . . . . .	138
Reducing oils . . . . .	94, 130
References . . . . .	194
Rosin . . . . .	129
Rosin oil . . . . .	129
Outerbridge test for . . . . .	127
Rosinates . . . . .	134
colloidal formation of . . . . .	135

## S

Separation of oil for determination of its constants . . . . .	101
Separation of pigment . . . . .	97
Separation of vehicle from pigment . . . . .	96
Shellac, adulteration of . . . . .	173
insoluble test for . . . . .	174
iodine absorption of . . . . .	173
substitutes . . . . .	179
valuation of . . . . .	167
varnishes body of . . . . .	167
detection of rosin in . . . . .	168
estimation of rosin in . . . . .	170
Solvent naphtha . . . . .	50
Soya bean oil . . . . .	91, 129
analytical constants of . . . . .	92
uses of . . . . .	91
Specification paints . . . . .	121
Specific gravity . . . . .	122
Spot test . . . . .	125
Standard Engler flask . . . . .	17
Stearine pitches . . . . .	158
Sulphonation test . . . . .	151
Sulphurized oils . . . . .	187

## T

Thermometer readings, correction for . . . . .	125
Tung oil, acid value of . . . . .	82
anomalous dispersion of . . . . .	80

	PAGE
Tung oil, constitution of . . . . .	80
domestic . . . . .	84
effect of climatic influence on . . . . .	83
heating test for . . . . .	87
iodine jelly test . . . . .	88
iodine number of . . . . .	86
normal purity of . . . . .	82
refractive index of . . . . .	86
regulations of New York Exchange . . . . .	89
specifications for . . . . .	84
specific gravity of . . . . .	84
unsaponifiable matter in . . . . .	85
valuation of . . . . .	79
variation in composition of . . . . .	82
Turpentine . . . . .	112
density of . . . . .	30
distillation of . . . . .	29
polymerization . . . . .	31
refractive index of . . . . .	29
specifications for . . . . .	28
U	
U. S. Bureau of Mines Flash Tester . . . . .	26
V	
Varnish, determination, of metallic driers in . . . . .	181
of volatile thinners in . . . . .	180
esterification of . . . . .	183
identification of gum constituents . . . . .	191
kauri test . . . . .	192
separation of, gum constituents . . . . .	190
oil acids . . . . .	189
oil and resin . . . . .	181
unsaponifiable in . . . . .	182
Volatile thinners, definition of . . . . .	115
estimation of . . . . .	116
aromatic hydrocarbons . . . . .	117
increase in use of . . . . .	115
loss in varnishes . . . . .	121
loss in grinding . . . . .	119
Volume equivalents . . . . .	196
W	
Walker and Wertz method . . . . .	62
Water, combined . . . . .	106

	PAGE
Water, in containers.....	106
determination of.....	107
estimation of.....	105
occurrence in paints.....	105
Wijs solution.....	171
Wood alcohol.....	35
impurities in.....	35
Wolf's esterification method.....	183

## Z

Zinc oxide.....	138
Zinc soaps.....	134
Zinc sulphate.....	138











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